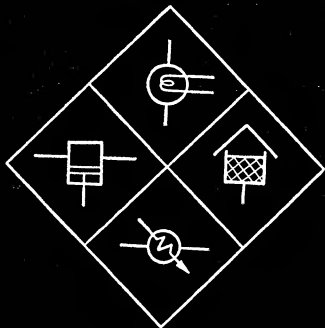


ATTACHMENT A

Cryogenic Engineering



Edited by
B.A.HANDS

ORE

438929

TP 482.C74

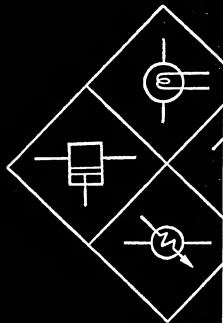
1986

10PY 1

HANDS

Cryogenic Engineering

Cryogenic Engineering



Edited by
B.A.HAN

0.12.322990.1

TP
482-
C74

1986

YORE 1

Cryogenic Engineering

Edited by

B. A. Hands

*Department of Engineering Science, University of Oxford,
and St. Hilda's College, Oxford, England*

1986



Academic Press

Harcourt Brace Jovanovich, Publishers

London Orlando New York San Diego Austin
Boston Tokyo Sydney Toronto

ACADEMIC PRESS INC. (LONDON) LTD.
24/28 Oval Road, London NW1 7DX

United States Edition published by
ACADEMIC PRESS, INC.
Orlando, Florida 32887

Copyright © 1986 by
Academic Press Inc. (London) Ltd.

All rights reserved. No part of this book may be reproduced
or transmitted in any form or by any means, electronic or
mechanical, including photocopy, recording, or any
information storage and retrieval system without permission
in writing from the publishers

British Library Cataloguing in Publication Data

Cryogenic engineering.
I. Low temperature engineering
I. Hands, B.A.
621.5'9 TP482

ISBN 0-12-322990-1
ISBN 0-12-322991-X (Pbk)

Computer typeset and printed by
Page Bros (Norwich) Ltd

C. A. Bail
eering S
and Fell
R. A. Byrr
Formerl
Californ
D. Dew-H
versity c
versity C
D. Evans
OQX, Ei
E. J. Grege
Fordhou
B. A. Hanc
eering So
and G.E
G. Krafft
Karlsruh
J. T. Morj
OX11 0C
N. Nambud
Bombay
Engineer
B. W. Riel
inghamsh
J. M. Roben
Establish
H. Sixsmitt
Hampshi
W. L. Swit
Hampshi
W. J. Tallis
Science, I
R. M. Tho
Chemical
T. J. Webst
England.

Contributors

- C. A. Bailey** University Lecturer, Cryogenics Laboratory, Department of Engineering Science, University of Oxford, Parks Road, Oxford OX1 3PJ, England and Fellow of Keble College, Oxford
- R. A. Byrns** Consultant, 2457 Marin Avenue, Berkeley, California 94708, U.S.A. *Formerly* Staff Senior Scientist, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720, U.S.A.
- D. Dew-Hughes** University Lecturer, Department of Engineering Science, University of Oxford, Parks Road, Oxford OX1 3PJ, England and Fellow of University College, Oxford
- D. Evans** Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, England
- E. J. Gregory** Chief Process Engineer, Marston-Palmer Limited, Wobaston Road, Fordhouses, Wolverhampton WV10 6QJ, England
- B. A. Hands** Research Associate, Cryogenics Laboratory, Department of Engineering Science, University of Oxford, Parks Road, Oxford OX1 3PJ, England and G.E.C. Lecturer in Engineering, St. Hilda's College, Oxford
- G. Krafft** Koordinationstelle Technologietransfer, Kernforschungszentrum Karlsruhe GmbH, Postfach 3640, D-7500 Karlsruhe 1, West Germany
- J. T. Morgan** Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, England
- N. Nambudripad** Tata Institute of Fundamental Research, Homi Bhabha Road, Bombay 400 005, India. *Formerly* of the Cryogenics Laboratory, Department of Engineering Science, University of Oxford
- B. W. Ricketson** Cryogenic Calibrations Limited, Pitchcott, Aylesbury, Buckinghamshire HP22 4HT, England
- J. M. Robertson** Heat Transfer and Fluid Flow Service, Atomic Energy Research Establishment, Harwell, Oxfordshire OX11 0RA, England
- H. Sixsmith** Creare Inc., PO Box 71, Great Hollow Road, Hanover, New Hampshire 03755, U.S.A.
- W. L. Swift** Creare Inc., PO Box 71, Great Hollow Road, Hanover, New Hampshire 03755, U.S.A.
- W. J. Tallis** Design Engineer, Cryogenics Laboratory, Department of Engineering Science, University of Oxford, Parks Road, Oxford OX1 3PJ, England
- R. M. Thorogood** Director, Cryogenic Research Programs, Air Products and Chemicals Inc., PO Box 538, Allentown, Pennsylvania 18105, U.S.A.
- T. J. Webster** Consultant, 38 Parkland Grove, Ashford, Middlesex TW15 2JR, England. *Formerly* Safety Manager, British Oxygen Company Ltd., England

Preface

The 1960s saw great activity in the field of cryogenic engineering, stimulated particularly by the American space effort and by developments in superconductivity. As a result, a number of books on cryogenic engineering in general were published. Since then, most volumes have concentrated on a particular aspect of the subject, rather than attempting a comprehensive review. In view of the steady, if unspectacular, advances made since that time, it seems opportune to attempt a new account of the basic science and of the engineering methods employed.

Cryogenic engineering covers a wide spectrum of disciplines, in traditional terms embracing much of electrical, mechanical and chemical engineering, its distinguishing feature being the use of temperatures well below ambient. In order to produce a volume of reasonable length, it was decided to assume that the reader should have knowledge appropriate to that of a final-year or graduate engineer or physicist. Further, since much of the body of knowledge of engineering at room-temperature can be applied directly to cryogenic problems, reference in such cases is made to standard textbooks, although since this book is biased towards engineering, the physicist may need to consult rather more of them than the engineer.

It was also decided, again on the grounds of overall length, to restrict the account of superconductivity. The design of superconducting magnets is very largely an electrical engineering problem, the cryogenic design, apart from training problems and stabilisation, being relatively straightforward. Further, the monograph "Superconducting Magnets" by M. N. Wilson (Oxford University Press, 1985) treats the subject comprehensively, and is required reading for anyone with other than a superficial interest in magnet design. Thus, the coverage of this topic is deliberately brief.

There are some other deliberate omissions, also. In particular, an account of refrigeration using hydrogen and neon is omitted, on the grounds that the techniques involved are broadly the same as those used for helium. Similarly, the particular problems involved with cryogenics in space are given only passing mention, since most of the design principles involved are also applicable to earth-based equipment. There is no attempt to provide complete property data; general trends are indicated, and, it is hoped, enough references for the reader to locate detailed data as necessary. However, since the book is intended for potential (and practising) cryogenic engineers, details of practical methods and current practices have been included.

The production of this book has been a co-operative effort, and I thank the authors for their tolerance of the editor's quirks. I should like to acknowledge those who have read parts of my own contributions and assisted with the provision of information, photographs and diagrams, particularly Dr A. Acton, Dr V. D. Arp, Mr R. J. Allam, Dr C. A. Bailey, Dr M. L. Christie, Dr. G. Davey, Prof G. B. Donaldson, Mr R. Harper, Dr D. B. R. Kenning, Dr R. D. McCarty, Dr W. Obert, Dr. C. Ruiz, Dr L. Solymar and Dr. R. M. Thorogood. Acknowledgements and sources for diagrams and photographs are given as appropriate in the text; I am most grateful to the organisations which supplied these and gave permission for their use. I am indebted to Johanne Beaulieu for preparing much of the text, to Mrs Judith Takacs for drawing the diagrams with her usual patience and skill, and to Mrs Stella Seddon for preparing the index. Finally, gratitude is due to my family for their tolerance, and for foregoing the use of the dining table for many months.

Oxford, 1985

B. A. Hands

In the tables of data, a dash indicates that information was not available.

Contributors
Preface

1.1 Introd
1.2 The C
1.3 Featu
1.4 Lique
1.5 Air Se
1.6 Liquic
1.7 Liquic
1.8 Super
1.9 Cryog
1.10 Cryog
1.11 Medic
1.12 Cryop
1.13 Instru
Refer
Journ
Gener
Bibliog
Non-s

2.1 Introd
2.2 Proper
2.3 Hydrog
2.4 Helium
2.5 Equatic

PREFACE

and I thank the
knowledge those
the provision of
Dr V. D. Arp,
by, Prof G. B.
Carty, Dr W.
acknowledgements
in the text; I
permission for
of the text, to
and skill, and
e to my family
many months.

A. Hands

able.

Contents

Contributors
Preface

v
vii

1. A Survey of Cryogenic Engineering

B. A. Hands

1.1 Introduction	1
1.2 The Cryogenic Temperature Range	2
1.3 Features of Cryogenic Engineering	3
1.4 Liquefied Natural Gas (LNG)	6
1.5 Air Separation	10
1.6 Liquid Hydrogen	15
1.7 Liquid Helium	18
1.8 Superconducting Magnets and Machinery	19
1.9 Cryogenic Electronics	26
1.10 Cryogenics in Space	29
1.11 Medical and Biological Applications	29
1.12 Cryopumping	30
1.13 Instrumentation	33
References	34
Journals	36
General Bibliography	36
Bibliography of Specific Topics	36
Non-specialist Reading	37

2. Properties of the Cryogenic Fluids

B. A. Hands

2.1 Introduction	39
2.2 Property Data	40
2.3 Hydrogen	43
2.4 Helium	46
2.5 Equations of State	50

2.6 The Two-phase Region	54	5.9
2.7 Computer Packages	56	5.10
2.8 Approximate Equations	58	5.11
2.9 Properties of Mixtures	59	5.12
References	63	5.13
Sources of Data	63	5.14

3. Cryogenic Safety

T. J. Webster

3.1 Introduction	67	
3.2 Organisation for Safety	68	6.1 I
3.3 Relationship between Fluid Properties and Safety	68	6.2 I
3.4 First Aid	76	6.3 I
3.5 Combustion	77	6.4 I
3.6 Oxygen Hazards	79	6.5 I
3.7 Unexpected Hazards	83	6.6 I
3.8 Fluorine Safety	87	I
Bibliography	87	

4. Thermal Design

C. A. Bailey and B. A. Hands

4.1 Conservation of Energy Considerations	89	7.1 I
4.2 General Energy Requirements	90	7.2 I
4.3 Specific Heat	93	7.3 I
4.4 Thermal Contraction	97	7.4 I
4.5 Thermal Conductivity of Solids	100	F
4.6 Conduction through Gases	106	
4.7 Radiative Heat Transfer	107	
4.8 Thermal Insulations	112	
4.9 Applications to Design	116	
References	121	
Bibliography	121	

5. Fluid Dynamics

B. A. Hands

5.1 Introduction	123	8.1 D
5.2 Pressure Drop Calculations	124	8.2 R
5.3 Single-phase Pressure Drop	125	8.3 C
5.4 Characteristics of Two-phase Flow	128	8.4 P
5.5 Two-phase Pressure Drop	130	R
5.6 Critical (Choked) Flow	131	9.1 I
5.7 Cooldown Behaviour	131	9.2 S
5.8 Introduction to Instabilities	132	9.3 F

CONTENTS

54
56
58
59
63
63

CONTENTS

- 5.9 Density Wave Oscillations
 5.10 The Ledinegg Instability and Pressure-drop Oscillations
 5.11 Geysering
 5.12 Thermoacoustic Oscillations
 5.13 Stratification, Thermal Overfill and Rollover
 5.14 Sloshing
 References

xi

134
136
138
141
143
146
148

6. Heat Transfer to Fluids

J. M. Robertson

67
68
68
76
77
79
83
87
87

- 6.1 Introduction
 6.2 Heat Transfer to Single-phase Fluids
 6.3 Heat Transfer Rates
 6.4 Pool Boiling
 6.5 Boiling in Channels
 6.6 In-tube Condensing
 References

151
153
156
157
160
166
168

7. Heat Transfer Below 10 K

G. Krafft

89
90
93
97
100
106
107
112
116
121
121

- 7.1 Introduction
 7.2 Basic Considerations
 7.3 Heat Transfer to Supercritical Helium
 7.4 Heat Transfer to Two-phase Helium
 References

171
172
174
181
191

8. Heat Exchangers

E. J. Gregory

- 8.1 Introduction
 8.2 Regenerators
 8.3 Coiled Tube Heat Exchangers
 8.4 Plate and Fin Heat Exchangers
 References

193
195
197
199
216

9. Electrical Conductors at Low Temperatures

D. Dew-Hughes

123
124
125
128
130
131
131
132

- 9.1 Introduction
 9.2 Simple Theory of Electrical Resistivity
 9.3 Real Conductors at Low Temperatures

217
219
221

9.4 Magnetoresistance	223	1
9.5 Superconductivity	225	
9.6 Theories of Superconductivity	229	
9.7 Flux-pinning and Critical Current Density	232	
9.8 Conductor Stability	235	13.1
9.9 Stress Effects	236	13.2
9.10 Commercial Superconductors	238	13.3
Bibliography	240	13.4
		13.5
		13.6
		13.7
		13.8
		13.9
		13.10
		13.11
 10. Mechanical Design with Metals		
B. A. Hands		
10.1 Introduction	241	
10.2 Elastic Moduli	242	
10.3 Plastic Behaviour	243	
10.4 Fracture Behaviour	246	
10.5 Fatigue Behaviour	252	
10.6 Aluminium Alloys	254	
10.7 Stainless Steels	257	
10.8 Nickel-Iron Alloys	262	14.1 Ir
10.9 Titanium Alloys	265	14.2 T
10.10 Copper Alloys	266	14.3 G
10.11 General Discussion	267	14.4 P
References	269	14.5 T
Bibliography	270	14.6 P
		14.7 C
		R
 11. Design with Non-metallic Materials		
D. Evans and J. T. Morgan		
11.1 Introduction	271	
11.2 Mechanical Properties of Polymers and their Relation to Structure	276	15.1 s
11.3 Thermal Contraction	285	15.2 I
11.4 Thermal Conductivity	289	15.3 "
Bibliography	292	15.4 I
		15.5 C
		15.6 I
		15.7 I
		15.8 C
		15.9 I
		15.10 I
 12. Construction and Assembly Methods		
W. J. Tallis		
12.1 General Design Considerations	293	15.11 I
12.2 Permanent Joints	295	15.12 "
12.3 Demountable Joints	302	15.13 I
12.4 General Comments	309	15.14 I

CONTENTS

223
225
229
232
235
236
238
240

241
242
243
246
252
254
257
262
265
266
267
269
270

271
276
285
289
292

293
295
302
309

CONTENTS

xiii

13. Principles of Refrigeration, Liquefaction and Gas Separation

C. A. Bailey and B. A. Hands

13.1 Refrigeration	313
13.2 Liquefaction	314
13.3 Cooling Methods	316
13.4 Simple Cycles	320
13.5 Irreversibility	324
13.6 Second Law Violations	324
13.7 Compound Cycles	325
13.8 The Separation of Gases	328
13.9 Principles of Distillation	329
13.10 The Single Column Linde System	336
13.11 The Double Column	339
References	340

14. Cryogenic Turbines and Pumps

H. Sixsmith and W. L. Swift

14.1 Introduction	341
14.2 Turboexpander Design	342
14.3 Gas Bearings	344
14.4 Protective Devices	348
14.5 Turbine Performance	349
14.6 Pumps	352
14.7 Conclusions	355
References	355

15. Large Helium Refrigeration and Liquefaction Systems

R. A. Byrns

15.1 Specification of Heat Load and Capacity	357
15.2 Design of J-T Stage	360
15.3 The Claude Cycle	362
15.4 Design and Optimisation	364
15.5 Compressors	366
15.6 Heat Exchangers	368
15.7 Expanders	369
15.8 Control, Instrumentation, Purity and Gas Management	371
15.9 Distribution and Cooling Methods	372
15.10 Large Helium Plants	375
15.11 Large Purification Liquefiers	375
15.12 The 1500 W Refrigerator	376
15.13 Lawrence Livermore National Laboratory (3000 W) System	379
15.14 Fermi National Accelerator Laboratory (23 kW) System	381

15.15 Brookhaven 24.8 kW Refrigerator	388
15.16 Refrigeration Equipment Cost	389
References	389

16. Large Gas Separation and Liquefaction Plants

R. M. Thorogood

16.1 Introduction	391
16.2 Cryogenic Air Separation Processes	392
16.3 Natural Gas Processes	409
16.4 Natural Gas Liquefaction Processes	411
16.5 Equipment for Large Air Separation Plants	418
16.6 Equipment for Natural Gas Plants	424
16.7 Operation and Safety	427
Acknowledgements	428
References	428

17. Small Refrigerators

N. Nambudripad

17.1 Introduction	431
17.2 The Stirling Refrigerator	433
17.3 The Gifford-McMahon Refrigerator	438
17.4 The Pulse-tube Refrigerator	441
17.5 The Vuilleumier Refrigerator	443
17.6 Losses in Regenerative Mechanical Coolers	445
17.7 Regenerators	447
17.8 Magnetic Refrigeration	452
References	453

18. Thermometry

B. W. Ricketson

18.1 Introduction	457
18.2 Temperature and Accuracy	458
18.3 Criteria for Choosing a Sensor	459
18.4 Sensors	460
18.5 Thermal Anchorage for Electrical Leads	467
18.6 Measurement	468
18.7 Temperature from the Measurement	473
18.8 Conclusion	476
References	476

Appendix	477
Index	485

CONTENTS

388
389
389

Symbols Used

391
392
409
411
418
424
427
428
428



Centrifugal Compressor



Aftercooler



Turbine Expander



Turbine Compressor



Reciprocating Compressor or Expander



Chiller



Turbine Expander with Electric Brake



Pump



Inlet Air Filter



Heater

431
433
438
441
443
445
447
452
453



Heat Exchangers Counterflow



Heat Exchangers Crossflow



Reboiler - Condenser



Distillation Column



Valve



Check Valve



Reversing Valve



Absorber



Vessel Containing Liquid

457
458
459
460
467
468
473
476
476

477
485

A Survey of Cryogenic Engineering

B. A. HANDS

1.1 Introduction	1
1.2 The Cryogenic Temperature Range	2
1.3 Features of Cryogenic Engineering	3
1.4 Liquefied Natural Gas (LNG)	6
1.5 Air Separation	10
1.6 Liquid Hydrogen	15
1.7 Liquid Helium	18
1.8 Superconducting Magnets and Machinery	19
1.9 Cryogenic Electronics	26
1.10 Cryogenics in Space	29
1.11 Medical and Biological Applications	29
1.12 Cryopumping	30
1.13 Instrumentation	33
References	34
Journals	36
General Bibliography	36
Bibliography of Specific Topics	36
Non-specialist Reading	37

1.1 Introduction

Most of this book is concerned with an outline of the theory and practice of cryogenic engineering. It has not been possible within a volume of reasonable size to explore every aspect in detail, nor has it been possible to give a detailed account of all the applications of cryogenics. This chapter is intended to give an impression of the wide range of cryogenic engineering. After a discussion of the meaning of cryogenics, the chapter covers the uses of the commoner cryogenic liquids (natural gas, oxygen, nitrogen, hydrogen and helium), and then deals with superconductivity and cryo-

pumping. The chapter concludes with a brief outline of cryogenic instrumentation.

1.2 The Cryogenic Temperature Range

The 1960s were a decade which saw a rapid expansion both in low-temperature physics and in the commercial exploitation of low-temperature techniques. Towards the end of this period, a need was felt for the standardisation of low-temperature terminology, and, on the initiative of Professor Nicholas Kurti, the Comité d'étude des termes techniques français organised a meeting in 1969, at which was formed a small international committee to consider the terminology of low temperatures, remembering the necessity of unambiguous translation between English and French, and paying due regard to current practice in the United States. As an example of the confusion which then existed, temperature levels in Britain were, by some people, referred to as 'low' (below 0°C), 'very low' (around 100 K), 'deep low' (around 4 K) and 'ultra low' (less than 0.3 K), although the French had only two terms 'basse' and 'très basse'. It was never clear how the British users of this terminology would refer to temperatures in the microkelvin region!

The working group, with members from six countries, made its recommendations in 1971 [1.1], and these have largely been accepted by the scientific community. 'Cryogenics' and the corresponding prefix 'cryo' were to refer to 'all phenomena, processes, techniques or apparatus occurring or used at temperatures below 120 K' approximately, that is, around or below the normal boiling point of liquefied natural gas. It was recognised, however, that some inconsistencies were unavoidable, in particular the use, on historical grounds, of the terms cryohydrate, cryoscopy, cryochemistry and the French cryodessiccation, all of which refer to temperatures well above 120 K; and, because they use cryogenic fluids and techniques, cryosurgery, cryomedicine and cryobiology. Otherwise, the temperature range between 120 K and 0°C is covered by 'refrigeration' technology.

The scientific community has, on the whole, adhered to these proposals, but they have not been rigidly adopted by industry, where the technology of handling liquid ethylene (at around 150 K) is, with some justification on the grounds of the equipment used, included in the cryogenic domain, and 'cryogenic' is also used, with less justification, to describe equipment designed for use at still higher temperatures. However, since all fluids and materials used in cryogenics must at some time be brought to room temperature, properties and processes in the temperature range up to room temperature cannot be ignored.

1. A SURVEY OF CRYOGENICS

In this book, we use the word 'engineering' to refer to the most widely used liquid liquefied natural gas liquid hydrogen (LH) importance of hydro range, the product regarded as 'physics' at present to experiment demagnetisation and be covered in this volume.

1.3 Features of Cryogenics

It is worth considering 'ordinary' (or room temperature) that the properties of a particular material accepted that, in fact, behave similarly to cryogenics the use of low temperature different from that of room temperature design criteria with identification of methods to achieve cryogenics should, therefore, be in its own right.

There are, however, engineering temperature ranges—fluidity—the ability of a material to flow. The superfluid state has been achieved. The other phenomena of electrical resistance different for each material.

The other phenomena of electrical resistance different for each material.

* According to [1.1], the wide acceptance.

in low-temperature
the stand-
of Pro-
s français
ernational
embering
ench, and
example
were, by
id 100 K),
ough the
clear how
res in the

de its re-
ted by the
ryo' were
occurring
around or
cognised,
ar the use,
chemistry
tures well
ues, cryo-
ture range

proposals,
echnology
ication on
main, and
equipment
all fluids
t to room
up to room

In this book, we follow the 1971 recommendation and take 'cryogenic engineering' to refer to the temperature range below about 120 K. The most widely used liquids, in order of descending normal boiling point, are liquefied natural gas (LNG), liquid oxygen (LOX), liquid nitrogen (LIN), liquid hydrogen (LH₂) and liquid helium (LHe), although at present the importance of hydrogen has declined. At the lower end of the temperature range, the production of temperatures less than about 1.5 K may be regarded as 'physics' rather than 'engineering', since their use is restricted at present to experimental work. Therefore, techniques such as adiabatic demagnetisation and the use of the light isotope of helium (He³) will not be covered in this volume.

1.3 Features of Cryogenic Engineering

It is worth considering at this stage the differences between cryogenic and 'ordinary' (or room temperature) engineering. For a long time, it was felt that the properties of cryogenic fluids were in some way peculiar, so that a particular mystique arose around this area of engineering. It is now accepted that, in fact, cryogenics (with the exception of superfluid helium) behave similarly to other fluids, and that the art of cryogenics lies in the ability to recognise and cater for the particular problems which arise through the use of low temperatures *per se*. This requirement is, of course, no different from that required in any other branch of engineering: an assessment of design criteria and possible causes of equipment failure, together with identification of the best techniques, materials and construction methods to achieve safe, efficient and reliable operation. Cryogenics should, therefore, be regarded more as a special art rather than as a subject in its own right.

There are, however, two phenomena peculiar to the cryogenic engineering temperature range which merit special consideration. One is superfluidity—the ability of liquid helium to behave as if it has zero viscosity. The superfluid state has been investigated by both experimental and theoretical physicists for many years, and a deep understanding of its behaviour has been achieved. From the engineer's point of view, it is of interest because of the very high rates of heat transfer which can be attained.

The other phenomenon is that of superconductivity,* the complete loss of electrical resistance below some well-defined temperature which is different for each metal. Superconductivity is of increasing technical import-

* According to [1.1], the proper term is superconduction, but this word has never achieved wide acceptance.

ance in the provision of high and very stable magnetic fields, and its application to heavy electrical engineering is being extensively studied. In 1962, the discovery of the Josephson effect opened the door to a new range of superconducting electronic devices.

The penalty of operating in the cryogenic temperature range is that work must be done to reach and maintain the low temperature required; from the second law of thermodynamics, it is clear that the work will increase roughly in inverse proportion to the magnitude of the absolute temperature. For instance, to extract 1 J of heat reversibly at 77 K requires about 3.7 J of work, while to extract 1 J at 4.2 K requires about 68 J of work. In practice, of course, reversibility cannot be achieved, and the work actually required is somewhat larger, by a few tens of percent at the higher cryogenic temperatures, to a factor of ten in the liquid helium range. Thus, on economic grounds there is every incentive to avoid the use of cryogenics wherever possible.

Cryogenics can be considered to have been born towards the end of 1877, when the first liquefaction of oxygen was achieved, by Raoul Pictet in Geneva, Switzerland, and by Louis Cailletet in Chatillon-sur-Seine in France.* Each used a different technique. Pictet's was to cool oxygen at 470 bars to about 140 K using successively liquid sulphur dioxide and solid carbon dioxide, at which temperature he allowed the oxygen to escape through a valve, and saw a mixture of liquid and vapour in the resulting jet. Cailletet, on the other hand, cooled his oxygen to only -29°C using liquid sulphur dioxide, and then performed an adiabatic expansion to form a mist of droplets in his glass vessel. It is perhaps of interest to observe that Pictet's method of 'cascade' cooling followed by Joule-Thomson expansion is still used in many designs of refrigerator and liquefier, although usually in association with external-work machines.

The next significant step was the invention of the vacuum flask by James Dewar, which enabled liquefied gases to be stored for long periods and paved the way for the liquefaction of hydrogen and helium. Until Dewar's invention, the liquids were stored in the innermost of a number of concentric vessels, each containing in turn a boiling liquid of higher temperature. The vacuum insulated, glass flask is now well known to the general public as a 'Thermos'; in the scientific community the name 'dewar' is preferred and is also used for small storage vessels of metallic or polymeric construction.

Developments during the next two decades proceeded apace, with Claude in France and Linde in Germany developing techniques for the liquefaction and fractional distillation of air to produce oxygen and nitrogen, and

* Which scientist was first is of no concern to us here, nor is the ensuing controversy, which has been discussed recently by Kurti [1, 2].

1. A SURVEY

forming coi
today to m
the 'perma
afterwards
above the li
plentiful su
Leiden for
especially fo

Between 1
production
process of 'a
100 m³ (100
was still a co
duction being
basis, and the
the world.

Immediate
Massachusset
liquefier usin
making liquid
the same tim
during the 19
comparatively

As a result,
produced in q
conducting ma
was readily ava
those research
since the savin
water-cooled s
As confidence
constructed, so
tens of superco
refrigerators in
engines were d
several kilowatt

As to the futu
argon by the frac
process for man
present forms a v
in importance as
are developed. H

olds, and its
y studied. In
a new range

is that work
quired; from
will increase
emperature.
about 3.7 J
of work. In
ork actually
er cryogenic
e. Thus, on
f cryogenics

the end of
Raoul Pictet
sur-Seine in
d oxygen at
de and solid
n to escape
he resulting
-29°C using
sion to form
observe that
n expansion
ugh usually

sk by James
periods and
til Dewar's
f concentric
ature. The
l public as a
ferred and
onstruction.
with Claude
liquefaction
rogen, and

roversy, which

forming companies which are still in the forefront of cryogenic engineering today to market their inventions. Finally, in 1908, helium, the last of the 'permanent' gases, was liquefied by Kamerlingh Onnes, who shortly afterwards produced superfluid helium by reducing the vapour pressure above the liquid using a vacuum pump. It is worth noting, in these days of plentiful supplies, that Onnes's helium was painstakingly extracted at Leiden from large quantities of monazite sand imported from India especially for the purpose.

Between the two World Wars, there was a steady development in the production of oxygen and nitrogen by the distillation of liquid air (the process of 'air separation'), and during the 1930s plants producing around 100 m³ (100 t) of liquid oxygen per day were in operation. Liquid helium was still a comparatively rare and expensive commodity, the rate of production being limited to a litre or two per hour, often only on an intermittent basis, and the liquid being available in only very few laboratories throughout the world.

Immediately after the Second World War, Professor Sam Collins, at the Massachusetts Institute of Technology, developed a new design of helium liquefier using reciprocating expansion engines, which was capable of making liquid on a continuous basis at a rate of several litres per hour. At the same time, the extraction of helium from natural gas wells, begun during the 1920s, had greatly increased, so that helium gas, although still comparatively expensive, was no longer a rare commodity.

As a result, when, during the 1960s, Type II superconducting wire was produced in quantity on a commercial basis, enabling high-field superconducting magnets to be constructed for the first time, liquid helium was readily available for cooling. This development was quickly exploited by those research establishments concerned with high-energy nuclear physics, since the saving in energy costs compared with those of an equivalent water-cooled system quickly outweighed the much higher capital cost. As confidence was gained, magnets of increasingly complex design were constructed, so that each of the major laboratories now contain several tens of superconducting magnets. In parallel with these developments, refrigerators incorporating expansion turbines rather than reciprocating engines were developed; a number of refrigerators capable of extracting several kilowatts at 4 K have now been built.

As to the future, it is clear that the production of oxygen, nitrogen and argon by the fractional distillation of liquid air will remain a major industrial process for many years. The transport of liquefied natural gas by sea at present forms a vital link in the world's fuel supply system, but will decrease in importance as supplies of natural gas diminish and other energy sources are developed. Hydrogen may well be one of these fuels, but at present in

energy terms it is expensive to produce, requiring large amounts of primary energy, and the liquefaction process also consumes much energy. Liquid hydrogen, therefore, may never be economically viable as a fuel other than for a few specialised applications.

Superconducting magnet technology has assumed great importance, and since it is economically attractive compared with the use of conventional magnets and can also produce more uniform and time-invariant fields, applications are expanding. For a number of years, superconducting magnets have been routinely manufactured for experimental work in physics and chemistry, notably for nuclear magnetic resonance (NMR) and electron spin resonance (ESR). These methods have recently been extended to biological applications and now to medical diagnosis. This latter provides the first truly large-scale, commercial application of superconductivity.

Although superconducting motors, generators, transmission lines, and so on have been under active development in a number of countries, the scenario so far has been that each advance in superconducting electrical engineering has been matched by an advance in the corresponding room-temperature technology. Since the latter is usually less complex, it has been more attractive on the grounds of both cost and reliability.

In electronic engineering, the Josephson effect opened new prospects in the precise determination of voltage, in the measurement of very small magnetic fields and in rf applications. Devices based on the Josephson effect are now used on a routine basis.

Thus, although cryogenics is a field of relative antiquity, there has been an unusually long time between the discovery of some phenomena and their commercial exploitation. This was particularly so in the case of superconductivity, which was discovered in 1911 but only ceased to be a laboratory curiosity some 50 years later. On the other hand, devices using the Josephson effect were marketed within a few years of its prediction and discovery.

1.4 Liquefied Natural Gas (LNG)

Natural gas is typically composed of 85–95% methane, the remainder being mainly nitrogen, ethane, propane and butane, although quantities of heavier hydrocarbons, carbon dioxide, water, sulphur compounds and, occasionally, mercury, may also be present, the precise composition depending upon the reservoir from which it is extracted. Certain sources, notably in Kansas, are comparatively rich (about 0.4%) in helium and are the major sources of this element. Natural gas is extracted by drilling in a way similar to that used for oil production and is somewhat refined before

1. A SUR

use: the
or as liq
reduced.Natur:
century
pipeline
of Amer
relied on
of Japan
Europe

—

Y

—

19

19

19

19

19

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

amounts of primary
uch energy. Liquid
as a fuel other than

at importance, and
use of conventional
ne-invariant fields,
erconducting mag-
tal work in physics
NMR) and electron
been extended to
This latter provides
perconductivity.
mission lines, and
er of countries, the
nducting electrical
rresponding room-
omplex, it has been
ility.
ed new prospects in
ment of very small
l on the Josephson

ity, there has been
ne phenomena and
so in the case of
only ceased to be a
hand, devices using
of its prediction and

ine, the remainder
though quantities of
r compounds and,
recise composition
d. Certain sources,
i) in helium and are
cted by drilling in a
what refined before

use: the heavier hydrocarbons are separated as natural gas liquid (NGL) or as liquefied petroleum gas (LPG), and the nitrogen content may be reduced.

Natural gas was used on a local basis in the United States during the 19th century for both fuel and heating; by the 1940s it was being distributed by pipeline throughout much of the country and now provides about a quarter of America's energy requirements. Since about 1975, Great Britain has relied entirely on natural gas for its gas supplies; it forms a significant part of Japan's energy consumption; and its use is widespread throughout Europe and the USSR (Table 1.1).

Table 1.1
Past and Projected Consumption of LNG (10^6 t/year)*

Year	Japan	United States	Western Europe	Total
1975	5.0	0.25	8	13.3
1980	19	11	11	41
1985	44	39	22-36	105-119
1990	47-55	50-105	33-39	130-199

Sources of natural gas (10^6 t/year)*

	Americas	USSR	Middle East	Far East	Africa	Total
1980	1	—	3	15	22	41
1990	6-30	9-35	13-17	35-39	67-78	130-199

* From Thorogood [1.3].

Sources of natural gas are scattered relatively evenly around the globe, with the result that a trade has developed in transferring the gas to areas of large demand. Thus there are, for instance, major pipelines from Alaska southwards, and from the USSR to Western Europe. However, much gas is liquefied for both transport and storage to take advantage of the large decrease in specific volume which is achieved without the necessity for pressurisation.

The first shipments of LNG by sea were made on an experimental basis from Lake Charles, United States, to Canvey Island, England, during 1959, and as a result of the success of these voyages a regular service from Algeria to Canvey Island was instituted in 1961, carrying about 700,000 t/year. Twenty years later, routes had been established from Algeria and Libya to Europe, from Algeria to the United States, and from Alaska, Abu Dhabi,

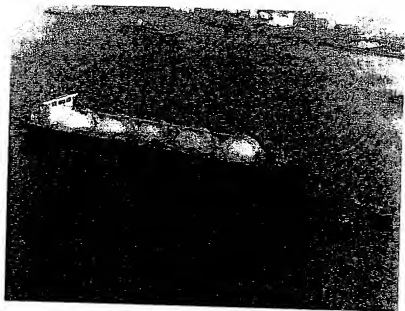
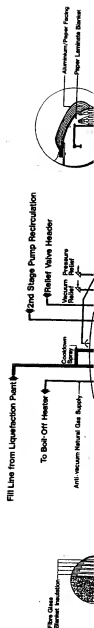


Fig. 1.1 The LNG tanker 'LNG Aquarius', launched in 1977, L.O.A. 285 m. The LNG is carried in 5 spherical aluminium tanks, each of 25,260 m³ capacity. (Courtesy of British Gas Corporation.)

Indonesia and Brunei to Japan, and another ten or so routes were under active development [1.4]. The shipping terminals are supplied by large liquefiers with up to 5000 t/day capacity in a single train (Fig. 16.22).

Apart from storage at liquefaction plants and trading terminals, natural gas is stored as liquid for 'peak shaving' operations, that is, to provide an additional source of gas during periods of peak demand when the normal supply system is inadequate (usually in winter). Liquefaction, using small (200 t/day) plants takes place during periods of low demand in the summer. Storage tanks may be as big as 100 m in diameter and 30 m in height, containing tens of thousands of tonnes of liquid (Fig. 1.2). In the past, they were usually constructed of either aluminium or 9% nickel steel; now, prestressed concrete (with a suitable thin metal liner to eliminate porosity problems) is being increasingly used. During the 1960s, a number of tanks were formed by excavating a hole in the ground and installing a thin steel liner, but this design has proved to be unsatisfactory due to large evaporation rates and to an ever-increasing area of frozen ground around the tank, although new designs are now being developed in Japan.



are under
by large
(.22).
; natural
provide an
e normal
ing small
summer.
a height,
ast, they
el; now,
porosity
of tanks
g a thin
to large
d around
n.

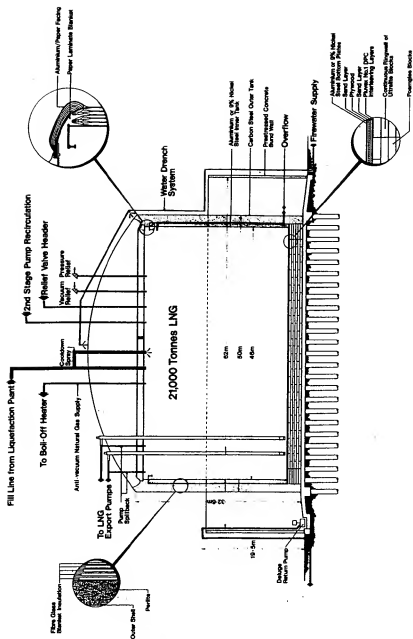


Fig. 1.2 A 50,000 m³ tank for the storage of liquefied natural gas for peak shaving. A bund is provided to retain the liquid in case of leakage. The insulated interspace, which contains natural gas vapour, is open to the vapour above the liquid, so that there will be no pressure differential. The horizontal ceiling above the liquid is insulated with glass fibre. The outer tank is designed as a pressure vessel, and in some designs might be reinforced concrete rather than carbon steel. (Courtesy of British Gas Corporation.)

Besides these large-scale facilities, in some areas it has proved economic to distribute LNG by truck and to keep it in small storage vessels close to the point of use. The technology adopted is similar to the well-established methods used for oxygen and nitrogen.

Purification ('upgrading') of natural gas is achieved by cryogenic methods. Many natural gas sources contain significant quantities of nitrogen and carbon dioxide, which reduce the calorific value and render the gas incompatible with other supplies to the pipeline distribution network. Upgrading plants are based on successive liquefaction and separation of the various components of natural gas and are frequently installed at the well-head. In these plants, solid impurities (sand, etc.) are filtered, and then water, sulphur compounds and carbon dioxide are removed using either molecular sieves or chemical absorption, for example, using glycol to absorb water or monoethanol amine to absorb carbon dioxide. Liquefaction can then take place without blocking the low-temperature heat exchangers with frozen components of the gas. Currently, natural gas companies are projecting a significant increase in the number and size of such plants. This increase is associated with the use of nitrogen injection into the gas wells to enhance gas recovery, thus creating a double use of cryogenics for both injection and rejection, since the nitrogen will be produced on-site by the fractional distillation of liquid air.

1.5 Air Separation

The production of oxygen, nitrogen and argon by the fractional distillation of air, or 'air separation' as it is known, forms a vital part of the infrastructure of the industrialised world. The major developments have occurred since the Second World War: in 1948, a system to produce 140 t/day of liquid oxygen was built in the United States; in the 1970s, plants with ten times that capacity were under construction in various parts of the world. The daily world production of oxygen is now about 5×10^5 t (Fig. 1.3), a purity of around 99.5% being easily achievable even on this scale.

By far the greatest amount of oxygen is consumed by the chemical and steel industries (Table 1.2). Since the daily consumption of a chemical or steel works may amount to several hundred tonnes per day, it has become common practice to build an air separation plant on an adjacent site and deliver the oxygen by pipeline. Because a continuous supply is essential, stringent conditions may be imposed by the user, and emergency electrical generators and back-up storage vessels may have to be provided to guarantee a supply until faults can be rectified or oxygen brought in by road.

1. A SURV

Fig. 1.3 W

A consic
compresses
hospitals. C
oxidation o
methanol p
and in the ti

I
—
—
St

Nc
Fa
Ch
I
/
7
F
V
C

Pol.
Mis
—
r.

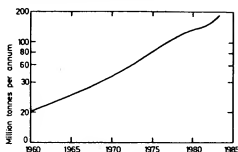


Fig. 1.3 Worldwide annual production rate of oxygen. (Courtesy of R. M. Thorgood.)

A considerable quantity of oxygen is produced in gaseous form and compressed into cylinders to be used, for instance, for welding, in diving and hospitals. Other important and growing uses for oxygen are in the partial oxidation of coal and heavy hydrocarbons to synthesise gas mixtures for methanol production and to produce hydrogen for ammonia production, and in the treatment of waste water by activated sludge processes. The use

Table 1.2
Industrial Consumption of Oxygen in the United States in 1979*

Percent of total consumption		
Steel making		
Basic oxygen process	39.6	
Open hearth process	9.3	
Electric furnace	1.7	
Cutting, welding, blast furnace air enrichment	14.8	
Total		65.4
Non-ferrous metals		3.0
Fabricated metal products		7.0
Chemicals		
Ethylene oxide	8.2	
Acetylene	3.8	
Titanium dioxide	2.8	
Propylene oxide	2.3	
Vinyl acetate	2.3	
Other	0.6	
Total		20.0
Pollution control		3.0
Miscellaneous		1.6

* From Thorgood [1.3].

of oxygen in the production of fuels from coal is expected to increase as oil reserves diminish, an important aspect of this being the very large consumption which will be required at an individual site, perhaps 20,000–30,000 t/day: the SASOL II complex which is operational in South Africa uses 15,000 t of oxygen per day.

Liquid oxygen is also produced in quantity for use in aerospace activities, both as a fuel oxidiser and for life support systems. The amounts required can be large: for instance, each Apollo flight to the moon consumed about 2000 t (Fig. 1.4), and the annual consumption of the American space programme at its peak was about 400,000 t [1.5].

At the same time as oxygen is separated from air, nitrogen is also, of

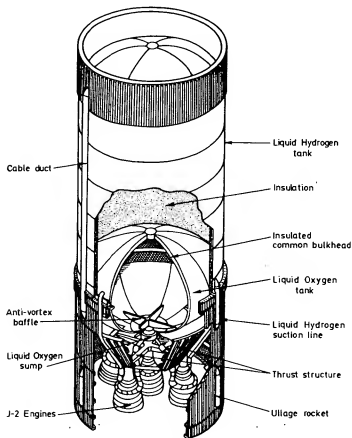


Fig. 1.4 Second stage of the Saturn V rocket launcher used for the Apollo flights to the moon. This stage was about 25 m high and 10 m diameter.

1. A SURVEY C

course, produ
oxygen. In th
by-product an
developed an
production.

Liquid nitro
cations, such :

- (1) for coc
tamination mu
- (2) for free
uses up to 700
- (3) in the
either side of
whole system;
- (4) in recli
of many meta
cold motor ve
constituents se
can be shattere
which does no
treated. In Bel
being fragment
- (5) in defla
deflashing can
each item indiv
- (6) in the t
resistance of ca
- (7) for the
the cattle indu
- (8) in astro
- (9) in grou
to be performe
- (10) in bon
porarily harmle

However, th
for various che
dependent upon
for such applica
and chemical i

course, produced, the current world-wide consumption being about that of oxygen. In the early years of the industry, nitrogen was considered a by-product and sold relatively cheaply. However, new uses have been developed and some plants are now biased more towards nitrogen production.

Liquid nitrogen is a useful source of cold and finds a diversity of applications, such as:

(1) for cooling cold traps in vacuum systems, especially where contamination must be avoided, as in semi-conductor device manufacture;

(2) for freezing food: one major fast-food franchise in the United States uses up to 700 t/day for freezing hamburgers;

(3) in the repair of pipelines: by freezing the liquid in the pipeline on either side of the fracture, a repair can be effected without emptying the whole system;

(4) in reclamation processes, where use is made of the embrittlement of many metals and polymers, at low temperatures, when, for instance, cold motor vehicle tyres can be pulverised, and the steel and polymer constituents separated and re-used; the polymer coating of electric cables, can be shattered into small pieces while the copper or aluminium conductor, which does not become brittle, remains intact. Large items can also be treated. In Belgium, for example, complete automobiles are cooled before being fragmented; it is claimed that the process reduces the overall energy consumption of the process and makes it easier to separate the ferrous from the non-ferrous (non-embrittled) scrap;

(5) in deflashing of moulded polymer products: in the embrittled state, deflashing can be achieved by a tumbling process rather than by treating each item individually;

(6) in the heat treatment of metals: for instance, to improve the wear resistance of certain tool steels;

(7) for the storage of biological specimens, especially bull semen for the cattle industry;

(8) in astronautics, for pre-cooling fuel tanks prior to filling with oxygen;

(9) in ground freezing, to enable tunnelling and excavation operations to be performed in wet and unstable soils;

(10) in bomb disposal, for freezing explosives to render them temporarily harmless.

However, the widest use for nitrogen is as an inert blanketing gas for various chemical and metallurgical processes. The purity required is dependent upon use, with medium purities (1-3% oxygen) being acceptable for such applications as blast furnace feed systems, coal handling systems and chemical tank purging. High purity (less than 10 ppm oxygen) is

essential for many purposes, of which steel annealing, float glass manufacture and fabrication of semi-conducting devices are important examples. Gaseous nitrogen is also used as a feedstock for the production of some chemicals, particularly ammonia. For large-scale uses, the nitrogen is supplied by an on-site plant or by pipeline. In other cases, it is often convenient to store the nitrogen as liquid rather than as gas in cylinders and vaporise it as required.

As already mentioned, a relatively recent and growing use of nitrogen is as a displacing medium in the recovery of oil and gas. By forcing oil or natural gas out of the well under pressure, a significant increase in the percentage extracted can be achieved. Such applications are of large volume and require delivery pressures between 130 and 700 bars.

The other major constituent of air is argon, which is in great demand for inert blanketing when nitrogen is too reactive, and for inert gas-shielded welding (TIG, MIG, etc.), although helium tends to be preferred in the United States. Because a very high purity (>99.9%) is required for most purposes, the impure product from several air-separation plants may be sent to a central point for purification. The air-separation industry is, in fact, so competitive that the recovery of argon may be necessary to prevent a plant running at a loss. The demand for argon is increasing rapidly, and it is possible that in the future some air-separation plants will be operated for the production of argon only, the nitrogen and oxygen being discarded. Although much argon is supplied as compressed gas, it is more economical for even moderate users to receive and store argon as liquid.

Of the minor constituents of air (Table 1.3), neon, krypton and xenon are extracted mainly for use in the lamp industry and laboratory instruments. It is not at present economic to recover helium due to its availability from LNG wells.

Table 1.3
Potential Yield of Atmospheric Rare Gases from a 1000 t/day Oxygen Plant*

	Total in air passing through plant (m ³ /hr at NTP)	Typical yield (%)	Cylinders per day
Argon	1395	55	2800
Neon	2.7	60	6
Helium	0.75	60	2
Krypton	0.17	30	0.2
Xenon	0.014	30	0.015

* From Thorogood [1.3].

1.6 Liquids

Hydrogen explosive (0.02 mJ a no unusua 1970s, whe Its importa for exampl

Hydroge hydrocarb gas or fuel scale, elec due mainl hydrocarb burning hy Electrolytic hydrogen. since it clea the resultin tigation of thermocher

Hydroge (Chapters 1 higher. A c and para (C conversion being usual Care must a oxygen whi believed, ca perature pa

Liquid hy nuclear phys a target for from the en to measure interactions. volume of li of a charged a piston in oi

1.6 Liquid Hydrogen

Hydrogen gas is a somewhat hazardous substance to handle due to its wide explosive concentration range with air (4–72%) and its low ignition energy (0.02 mJ at 30% concentration), although the liquid itself appears to present no unusual problems and was in wide use for cooling purposes until the 1970s, when liquid helium became more easily available in large quantities. Its importance as a cryogen has declined considerably since then, so that, for example, in Great Britain it is no longer commercially available.

Hydrogen gas is produced on a large scale by the reaction of steam with hydrocarbons, particularly natural gas, or by the partial oxidation of natural gas or fuel oil. The gasification of coal may also be used. On a smaller scale, electrolysis of water is used, in spite of its higher cost, which is due mainly to the higher binding energy of hydrogen in water than in hydrocarbons, to the high cost of electricity (itself often produced by burning hydrocarbons), and to the low efficiency of electrolytic cells. Electrolytic hydrogen may cost twice as much as the cheapest 'chemical' hydrogen. There is currently interest in developing hydrogen as a fuel, but since it clearly does not make sense to produce it from other fuels (with the resulting overall loss in available energy), there is widespread investigation of methods for producing hydrogen from water using various thermochemical methods.

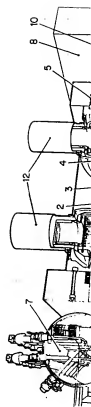
Hydrogen may be liquefied using cycles similar to those in use for helium (Chapters 13 and 15), except that the cycle pressures are about five times higher. A complication is that, because hydrogen exists in two forms, ortho and para (Chapter 2), the inclusion of catalysts to promote ortho-to-para conversion must be considered. Great care must be taken with safety, it being usual to provide a blast wall between the liquefier and its operators. Care must also be taken to free the hydrogen from impurities, especially oxygen which can promote unwanted ortho-para conversion, and, it is believed, cause an explosion if accumulated as solid in the lower temperature parts of the plant.

Liquid hydrogen still finds two particular applications. In high-energy nuclear physics experiments, liquid hydrogen or deuterium may be used as a target for the particles produced from the accelerator. More interesting from the engineering point of view is the bubble chamber, which is used to measure the properties of charged particles and to elucidate their interactions and decays. A bubble chamber consists essentially of a closed volume of liquid held at a pressure well above saturation. On the passage of a charged particle, the pressure is rapidly reduced, usually by means of a piston in one wall of the chamber, so that the liquid is in the superheated

state, and bubbles form along the track of the particle. A stereo photograph is taken, and the liquid is recompressed before bulk boiling occurs, the whole cycle taking a few tens of milliseconds. A large magnet surrounds the chamber so that the momentum of the particle can be deduced from the curvature of the track. Bubble chambers containing hydrocarbons and helium have been built, but hydrogen and deuterium are particularly favoured because their simpler nuclear structure allows a more straightforward interpretation of any interactions which occur. Hydrogen bubble chambers have been built as large as 3 m in length and containing several cubic metres of liquid, but they have now been superseded by other methods of detection, and the present tendency is to use smaller chambers surrounded by electronic detectors (Fig. 1.5).

The other application for which liquid hydrogen is still produced in quantity is as a fuel for space vehicles. When used with oxygen, it has a high propulsive energy per unit mass, and on this basis was, for instance, chosen for the fuel of the second and third stages of the rocket for the Apollo manned space flights to the moon, each of which consumed about 90 tonnes (1300 m³) of liquid hydrogen (Fig. 1.4); in the late 1960s, the American space programme was using about 40,000 t/year [1.5]. In the 1980s, each launch of the space shuttle consumes about 120 tonnes (1700 m³). Although on a mass basis hydrogen has a calorific value about three times higher than kerosene (which was used for the first stage of Apollo), its calorific value per unit volume is about three times lower. Thus rockets fuelled with hydrogen have to be much larger than those fuelled with kerosene, and this can entail problems of structural stability, particularly bending oscillations during flight.

There has been widespread discussion of the possibility of using hydrogen as a fuel for aircraft and automobiles as oil supplies diminish, although as already mentioned, a novel and energy-efficient means of producing hydrogen must be developed before this becomes a reality. On the question of safety, it can be argued that although hydrogen is more easily ignited than hydrocarbon fuels, its flame radiates little heat. Also, since hydrogen is lighter than air, it spreads upwards rather than outwards, so that overall there is probably little to choose between the two fuels. The storage of hydrogen is, however, a major problem. Storage as metal hydrides imposes a large weight and cost penalty because of the metals used and their low absorption capacity. Storage as liquid is clearly convenient, but requires large fuel tanks as mentioned earlier, although some saving in volume (about 15%) can be made by using a mixture of solid and liquid—'slush hydrogen'. Considerable care would have to be taken in the disposal of boil-off in a safe way. Perhaps a more serious drawback is the energy required for liquefaction, which may amount to as much as a third of the



B. A. HANDS

o photograph
g occurs, the
et surrounds
duced from
ocarbons and
: particularly
ore straight-
rogen bubble
ining several
led by other
er chambers

produced in
gen, it has a
for instance,
cket for the
umed about
e 1960s, the
[1.5]. In the
120 tonnes
value about
irst stage of
lower. Thus
fuelled with
particularly

ng hydrogen
h, although
f producing
he question
asily ignited
e hydrogen
that overall
: storage of
des imposes
d their low
ut requires
in volume
uid—slush
disposal of
the energy
hird of the

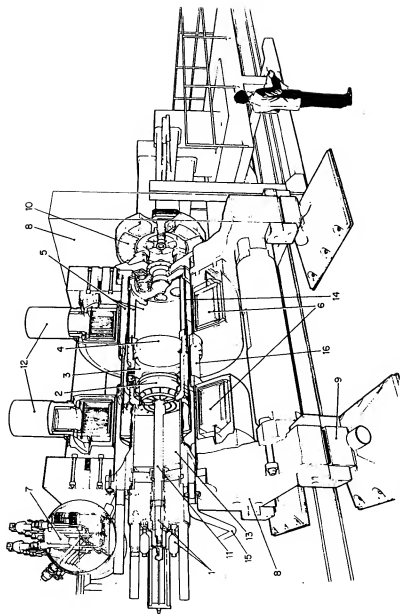


Fig. 1.5 Rapid-cycling hydrogen bubble chamber built for high-energy nuclear physics experiments. (1) Hydraulic actuator, (2) glass-reinforced plastic piston and bellows, (3) active volume (250 l), (4) main optical window, (5) vacuum enclosures, (6) superconducting magnet coils, (7) chamber refrigeration control vessel, (8) iron support structure, (9) damped mountings, (10) cameras and light-source assembly, (11) piston shaft, (12) magnet lead and transfer line enclosures, (13) thermal insulation, (14) radiation shield cooled by helium gas at 20 K, (15) safety vent and (16) outer vacuum vessel. (Courtesy of the SERC, Rutherford Appleton Laboratory.)

calorific value of the fuel liquefied. This, together with the present high cost of production from non-hydrocarbon sources, makes hydrogen economically unattractive, although several experimental automobiles have been successfully run with liquid hydrogen as fuel for a number of years.

1.7 Liquid Helium

The importance of helium to the physicist and cryogenic engineer is that it is the only route to temperatures below about 10 K, apart from magnetic cooling methods which are unlikely to become practical on anything but a very small scale. The provision of helium refrigeration is, therefore, a necessary adjunct to the use of superconducting magnets.

The largest sources of helium in the western world are currently the natural gas wells of the states of Texas and Kansas in the United States. Wells in Poland, Northern Germany and the USSR (at Orenburg) also produce large quantities. Helium is present in these wells at a concentration of about 0.2–0.7% and is extracted by liquefying the other constituents. Although at present there is plenty of helium available, there are worries that if the growth in both size and number of superconducting magnets continues at the present pace, there could be a severe shortage in a few decades as natural gas wells become exhausted, even though the United States has considerable quantities of helium stored in underground porous rock—a result of the so-called 'conservation' programme which has now been discontinued [1.6]. Outside America, 'conservation' has a rather different connotation—that of recycling the gas after use, rather than exhausting it to the atmosphere. Such recovery is usually justifiable on economic grounds alone, since gaseous helium is not cheap, but it is worth noting that large quantities are used in welding and in oxygen–helium atmospheres for diving, from which helium recovery is not feasible.

A major landmark in the development of helium technology came in 1946 with the design by Professor Sam Collins of a liquefier which did not require the feed helium to be pre-cooled and which could be operated continuously for long periods. Previous to this, small-scale experiments were done by liquefying helium *in situ*, for example, by precooling with liquid hydrogen (sometimes itself produced *in situ*) and then adiabatically expanding. Continuous liquefaction was achieved using cascade cooling with liquid air (or nitrogen) and hydrogen followed by Joule–Thomson expansion. The latter method could produce a few litres of helium per hour, but required the simultaneous operation of both a hydrogen and a helium liquefier, the liquid air or nitrogen usually being available from a commercial source.

1. A SURVEY OF

The Collins liquefier proved to be a means that fair still marketed to bearings were d liquefiers, and s refrigerators. The engine, have no high efficiency. liquefiers.

Another problem to compress the since all will free is especially imp to be run contin contamination is believed that w blockages in one received general based, piston rings, compressors, bearings, reciprocating components require a sophisticated refrigerator itself more frequent m for more massive contamination is sim

1.8 Superconduct

Perhaps the one has been the ex conductivity or the phenomenon was major part in elect was destroyed by presence of a magnetic field remained unfulfilled 'high-field' superconductors remain superconduct

present high
hydrogen econ-
omies have
been of years.

It is that it
on magnetic
anything but a
therefore, a

currently the
United States.
Lorenburg) also
concentration
constituents.
There are wor-
ries in mag-
nets age in a few
in the United
around porous
which has now
has a rather
rather than
justifiable on
at it is worth
hydrogen-helium
feasible.

Why came in
which did not
be operated
experiments
cooling with
adiabatically
ade cooling
le-Thomson
helium per
hydrogen and a
table from a

The Collins liquefier, which used a reciprocating expansion engine, proved to be a reliable machine, although the presence of rubbing seals meant that fairly frequent maintenance was required; its derivatives are still marketed today. During the 1950s, high-speed turbines running on gas bearings were developed as the external work components for hydrogen liquefiers, and soon afterwards this technique was incorporated in helium refrigerators. These turbines, although less robust than a reciprocating engine, have no rubbing surfaces and can achieve a large throughput at high efficiency. They are now usually specified for large refrigerators and liquefiers.

Another problem in the design of refrigerators arises from the necessity to compress the gas. The helium feed must be free of oil, water and air, since all will freeze at some point in the system and cause blockages: this is especially important today, when superconducting systems may have to be run continuously for many months. To achieve such service, oil contaminations less than 1 part in 10^7 may have to be specified, and it is believed that water contamination of about 3 parts in 10^8 has caused blockages in one system [1.7]. Two types of compressor appear to have received general acceptance, reciprocating compressors with dry, polymer-based, piston rings, and oil-flooded screw compressors. Oil-flooded screw compressors, being rotating machines, suffer from fewer problems than reciprocating compressors and are more compact and vibration-free, but require a sophisticated oil-removal system. Furthermore, it is not unknown for a malfunction to occur such that much of the oil is delivered into the refrigerator itself. Reciprocating compressors have the disadvantage of more frequent maintenance intervals, more vibration and a requirement for more massive foundations, but the equipment for removal of contamination is simpler.

1.8 Superconducting Magnets and Machinery

Perhaps the one major disappointment in the development of cryogenics has been the exploitation of the "electrical engineers' dream"—superconductivity or the complete absence of electrical resistivity. After this phenomenon was discovered in 1911, hopes persisted that it would play a major part in electrical engineering, even though the superconducting state was destroyed by the passage of a current of only a few amperes or the presence of a magnetic field of only a few tenths of a tesla, but the dream remained unfulfilled for some 50 years. In the late 1950s, a range of 'high-field' superconductors were discovered, so called because they would remain superconducting in fields of tens of tesla. Also, their critical tem-

peratures, instead of being at the most 9.25 K (niobium) were 5–10 K higher. It was discovered, however, that the construction of a superconducting magnet involved more than just winding the wire into a coil, and that copper had to be incorporated to 'stabilise' the magnet and allow it to operate at the fields which a short sample of the wire could sustain. In order to optimise the performance, many subtle techniques had to be learnt, and even today new designs are not always completely successful. Nevertheless, magnets are now made commercially on a production-line basis, and, for large magnets at least, at a cost less than their water-cooled copper equivalents, to which they are superior on running costs and in stability of field.

Superconducting magnets have found widespread applications in research



Fig. 1.6 Small superconducting magnet for research use. This is a split-pair magnet, wound partly from niobium-tin wire and partly from niobium-titanium, producing 10 T in a 70 mm bore. The maximum diameter is about 25 cm. The 12 resistors on top of the assembly are used to absorb energy should the magnet unexpectedly change from the superconducting to the normal state ('quench'). (Courtesy of Oxford Instruments Ltd.)

1. A SURV

laboratoric
cubic cent
of NMR a
use into ch
which the
coming into
nucleus (p
radiation, t
magnetic fi
between 0.
the x, y at
correlating
mation may
intensity of
Since the w
body, a 3-di
abnormalitie
lattice and
acquired. Th
(Fig. 1.7), w
and a stabilit

Still at a
Spectroscopy
nuclei due to
resonant freq
vivo. Process
tissue during
²³Na nucleus,
Because the π
of protons, m
No adverse
MRI or MRS.
field, which ca
necessary), an
ferrous objects

For MRS an
used, the latte
cryogenics for
environments.
conductivity, t
per year world
Large magn

(niobium) were 5–10 K construction of a superconducting the wire into a coil, 'ise' the magnet and allow of the wire could sustain. the techniques had to be ys completely successful. ally on a production-line s than their water-cooled on running costs and in d applications in research


laboratories. Small magnets, providing a uniform field over a few tens of cubic centimetres, are mainly used by physicists (Fig. 1.6); the development of NMR and ESR techniques for analytical purposes has extended their use into chemistry and biology [1.8], and more recently, into medicine, in which the technique known as MRI (Magnetic Resonance Imaging) is coming into routine clinical use. In MRI, the resonance of the hydrogen nucleus (proton) is stimulated by applying radiofrequency electromagnetic radiation, the resonant frequency being directly proportional to the applied magnetic field. The patient is subjected to a uniform magnetic field of between 0.5 and 1.5 T, upon which are superimposed small gradients in the x , y and z directions. By changing the applied rf frequency and correlating the resonant frequency with the local field, 3-dimensional information may be obtained. The primary information is obtained from the intensity of the resonance, which depends upon the local proton density. Since the water and lipid content is different in the various tissues of the body, a 3-dimensional image of the body structure may be produced and abnormalities such as tumours may be located. Measurement of the spin-lattice and spin-spin relaxation times enable further information to be acquired. The magnets for whole-body MRI require a bore of about 1.0 m (Fig. 1.7), with a field homogeneity as good as 0.1 ppm of the main field and a stability of 0.1 ppm per hour [1.8].

Still at a more experimental stage is MRS (Magnetic Resonance Spectroscopy). Slight variations in the local magnetic environment of the nuclei due to different chemical surroundings produce small shifts in the resonant frequency, and this enables chemical reactions to be followed *in vivo*. Processes which have been investigated include changes in muscle tissue during exercise using the ^{31}P nucleus, cellular biochemistry using the ^{23}Na nucleus, and the kinetics of enzyme reactions using the ^{13}C nucleus. Because the magnetic moments of these nuclei are much weaker than those of protons, magnetic fields of about 6 T are generally required.

No adverse physiological effects are believed to occur with the use of MRI or MRS. The main safety problems are control of the stray magnetic field, which can be limited by the use of iron shielding (some 20 t may be necessary), and the prevention of personnel from inadvertently carrying ferrous objects into the region of the stray field.

For MRS and MRI, both conventional and superconducting magnets are used, the latter giving superior resolution but requiring some expertise in cryogenics for its operation which may not be available in some hospital environments. This is the first large-scale, non-research use of superconductivity, the current production rate being several hundred magnets per year worldwide.

Large magnets have been used since the mid-1960s by high-energy



is a split-pair magnet, wound producing 10 T in a 70 mm on top of the assembly are from the superconducting to Ltd.)

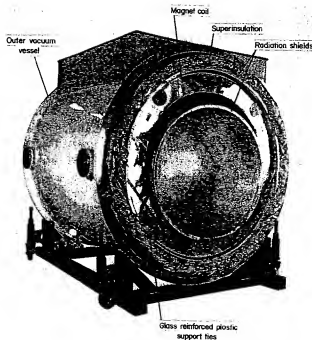


Fig. 1.7 A superconducting magnet, designed for whole-body scanning, during assembly. A field in the range 0.5–1.5 T is produced in a bore of 1 m. (Courtesy of Oxford Magnet Technology Ltd.)

nuclear physics establishments, at first for the focusing of ionised particle beams between the accelerator and the experiment, and lately in the accelerator itself. Such magnets are often one or two metres long with a bore of around 10 cm; besides simple solenoids, quadrupole and other configurations have been constructed. A great variety of superconducting magnets for other uses has now been made, for example, simple solenoids of several metres bore for use with bubble chambers; toroidal magnets for plasma physics experiments; and a 'yin-yang' configuration, weighing 341 t, for a nuclear fusion experiment (Fig. 1.8). Fields in the region of 10 T are commonplace, and some magnets are pulsed on a routine basis. High-energy nuclear physics and nuclear fusion have both given great stimulus to the development of magnet technology.

Applications in the generation and transmission of electric power have not been as successful, the enthusiasm of the manufacturers being counter-

1. A SURVEY

balanced by the story that has ahead of the mission line system would [1.10]. Ten temperature studies had transmitter continuously overload.

Similarly, construction power generated 1000–3000 M over conventional smaller by a at the most, reliable than therefore, the western programmes reported in 1 switched into construction

At present an electricity magnet capital substitution of Energy is tri controlled with supply [1.13] time of 10 m shaving' energy way as pump

There has most promise given power, generator is generally of rapid speed thus removing

balanced by the caution (realism?) of the utility companies [1.9]. In general, the story has been that advances in 'conventional' technology have remained ahead of the possibilities of using superconductors. Superconducting transmission lines are a good example. In 1973, it seemed that a superconducting system would be economically viable for powers greater than about 1 GVA [1.10]. Ten years later, due to advances in insulation technology of room temperature systems, the figure had risen to 5 or 10 GVA, and experimental studies had been largely abandoned, even though in 1984 the prototype ac transmission line at the Brookhaven National Laboratory [1.11] was run continuously for 4 weeks at 1 GW, and its stability demonstrated at 100% overload.

Similarly, in the 1970s there was considerable activity in the design and construction of models and prototypes of superconducting alternators for power generation aimed at eventual machines in the capacity range of 1000-3000 MW. Superconducting alternators have two major advantages over conventional designs: a greater efficiency, and a size and weight smaller by a factor of about two. However, the increase in efficiency is 1% at the most, and this is easily negated if the alternators prove to be less reliable than the machines currently in use. The generating authorities are, therefore, proceeding with extreme caution, and again by 1985, activity in the western world in this field had considerably diminished, with only small programmes remaining in the USA, Japan and Germany. However, it was reported in 1985 [1.12] that in the USSR, an experimental alternator was switched into the Leningrad supply in the summer of 1984, and that construction of 300 MVA alternators is proceeding.

At present, only one superconducting device is believed to be in use by an electricity supply authority in the western world. A superconducting magnet capable of storing 38 MJ of energy has been installed at the Tacoma substation of the Bonneville Power Administration in the United States. Energy is transferred between the magnet and the transmission line in a controlled way to damp out subsynchronous oscillations in the ac electricity supply [1.13]. An advantage of the system is the relatively fast response time of 10 ms. Much larger magnets have also been proposed as 'peak shaving' energy storage devices, which would be used in much the same way as pumped water storage is now.

There has been considerable interest in superconducting motors. The most promising application appears to be for ship propulsion, where, for a given power, a superconducting motor combined with a superconducting generator is much smaller than a conventional system. The motors are generally of the dc homopolar type. The small rotating mass facilitates rapid speed changes, and the motor will operate efficiently at low speed, thus removing the need for a gear box. However, on economic grounds a

conventional system is still superior, and the main use for a superconducting unit may be in naval vessels, for which flexibility and small size are important advantages, and in icebreakers, because of the frequent reversals of direction at low speed.

A different form of power unit is the linear motor, which, when combined with magnetic levitation, forms a suitable system for driving high-speed trains. Japanese National Railways has pursued such a development [1.14], intended for the commuter line between Kobe and Tokyo, which was predicted to reach full capacity soon after 1980. Work started in the 1960s, and the first prototype was successfully tested in 1975. Since then, the design has been considerably refined, and in 1979 the version known as ML-500 ran at 517 km/hr, a world record. Propulsion is by linear synchronous motor, the high-frequency ac power being provided by coils mounted on the track. Guidance and support are both achieved using a repulsive electromagnetic inductive method, which requires the train itself to be equipped with powerful magnets. In the Japanese system, each vehicle (28.8 m long and weighing about 10 t) is provided with eight superconducting magnets of 700 kA-turns each and on-board refrigeration (Fig. 1.9). Although the project is well advanced, there are no plans yet to introduce the train into commercial service, since passenger density on the line has increased slower than originally predicted.

Finally, one other use of superconducting magnets is showing commercial promise. In the 1960s, it was established that kaolin, which is used in paper-

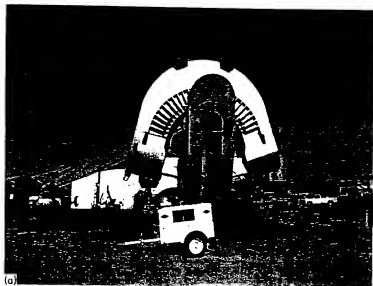


Fig. 1.8 (a) Opposite: Cc Laboratory. (b) diameter. The (re can also be seen photograph indic University of Cal Energy.)

HANDS
ducting
portant
of direc-

mbined
h-speed
[1.14],
ich was
1960s,
en, the
own as
achron-
ounted
pulsive
f to be
vehicle
super-
n (Fig.
yet to
on the

mercial
paper-



(b)

Fig. 1.8 'Yin-yang' magnet for the Mirror Fusion Test Facility in Berkeley, California.
(a) *Opposite*: Coil-box assembly (courtesy of University of California Lawrence Berkeley Laboratory). (b) Magnet during installation in the vacuum vessel, which is about 20 m in diameter. The (rectangular) end views of six cryopump modules for maintaining a high vacuum can also be seen, arranged radially around the top two-thirds of the vacuum vessel. This photograph indicates the complexity of a modern large cryogenic installation. (Courtesy of University of California Lawrence Livermore National Laboratory and U.S. Department of Energy.)

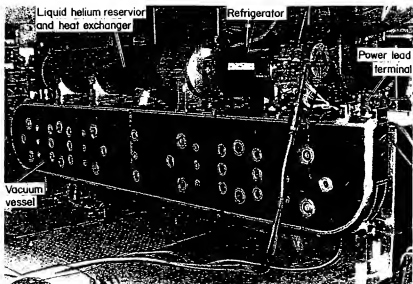


Fig. 1.9 A magnet-refrigerator assembly for the Japanese magnetically levitated train. The magnet coil is within the vacuum vessel. (Courtesy of Japanese National Railways.)

making, could be whitened by removing the discolourants, which are principally due to traces of iron, by passing the clay through a magnetic field gradient. Since then, applications have been found in the separation of ores, in the purification of chemicals, in the desulphurisation of coal and in the cleaning of flue gases and liquid effluents. The separation of red blood cells from plasma is also possible. Although many of these processes require only comparatively low magnetic fields, the use of superconducting magnets may be advantageous for certain applications [1.15].

1.9 Cryogenic Electronics

Many active electronic devices can be operated in a cryogenic environment [1.16]. They are generally of the field-effect transistor (FET) type and are based on silicon or gallium arsenide. For instrumentation purposes, there are clear advantages in placing at least some of the electronic circuitry close to the sensing head. However, there may also be inherent advantages in operating transistors at low temperatures, such as increased switching speed or lower noise. A serious problem is the effect on device reliability of the stresses induced by thermal cycling.

1. A SURVEY

Supercon-
two phenom
flux, which
more compl
extremely s
amount of t
Josephson e
lead or niob
oxide film at
such a layer
superconduc
superconduc
function of t
Josephson j
uncertainty i

The super
from a super
If the loop ei
because it is
wave func
there is a phi
hence of the

The rf SQ
loop, which i
drive a curre
measure of
Josephson j
through the J
current is th
Superconduc
nologies sir
methods may
dc SQUID i
be approach
a known dist
be measured

Among a
local anoma
and archaeol
routinely use
satellite tran
investigation



lower lead
terminal
fixed train.
always.)

uch are
agnetic
variation
oal and
of red
ocesses
ducting

nment
nd are
there
close
ges in
speed
of the

Superconducting electronic devices are in a different class. They rely on two phenomena—the Josephson effect and the quantisation of magnetic flux, which are described in a simple way in [1.17], for example, while a more complete account is given in [1.18]. The quantum of magnetic flux is extremely small: 2.07×10^{-15} Wb, which is approximately equal to the amount of the earth's field enclosed by a ring $10 \mu\text{m}$ in diameter. The Josephson effect is observed when two pieces of superconductor (commonly lead or niobium) are separated by a very thin insulating layer, perhaps an oxide film about 20 nm thick. Not only can single electrons tunnel through such a layer, but so can the pairs of electrons (Cooper pairs) to which superconductivity is attributed, so that the insulating layer behaves as a superconductor, although there is a discontinuity in the phase of the wave function of the Cooper pairs across the junction. The characteristics of the Josephson junction are now used to define the volt, and have enabled the uncertainty in the maintained standard to be reduced to about $0.1 \mu\text{V}$.

The superconducting quantum interference device (SQUID) is formed from a superconducting loop containing at least one Josephson junction. If the loop encloses some magnetic flux, there must be a circulating current because it is superconducting. This current consists of Cooper pairs whose wave functions form standing waves round the ring. Across the junction, there is a phase discontinuity which is a function of the current flowing and hence of the magnetic flux.

The rf SQUID is formed from a single junction in a superconducting loop, which is inductively coupled to a resonant circuit. This is arranged to drive a current round the loop, so that the voltage across the circuit is a measure of the magnetic flux being measured. In the dc SQUID, two Josephson junctions are made in the loop, and a dc current is passed through the parallel circuit so formed. The voltage required to produce the current is then a function of the magnetic field trapped inside the loop. Superconducting quantum interference devices may be fabricated by technologies similar to those used for integrated circuits, although other methods may also be used. The rf device is the easier to make and use; the dc SQUID is the more sensitive, and the quantum limit of sensitivity can be approached. By forming the superconducting loop from two rings with a known distance between their planes, small magnetic field gradients may be measured in the presence of a large uniform field.

Among a variety of applications, SQUIDS have been used to map local anomalies in the earth's magnetic field (of interest to geologists and archaeologists, for example) and for navigational purposes. They are routinely used as mixers and amplifiers for receiving weak signals from satellite transmissions, and are also used in infra-red detectors. In medical investigations, SQUIDS are used to record the varying magnetic fields

associated with bodily activity, the fluctuations ranging from 10^{-11} T (from the heart) down to 10^{-15} T (from the brain) [1.19]. Gradiometer arrangements are often used in an attempt to reduce to an acceptably low level the effects of local field fluctuations due to electrical equipment and ionospheric phenomena. Advantages over the use of ECG and EEG are that electrodes do not have to be attached to the patient, and that the measurements are localised rather than averaged over some distance. By spatial scanning, a 3-dimensional image of, for example, brain activity can be constructed and the position of a malfunction pin-pointed. With a single detector, such an image may take several days to produce, but attempts are being made to develop multiple arrays using several tens of SQUIDS to reduce the scanning time. It may be observed that whereas MRI (Section 1.8) gives information about the structure of tissue, these magnetic field measurements give information about the functional behaviour of the tissue. SQUIDS have also been used to detect accumulations of ferromagnetic material in various parts of the body.

Josephson junctions may be arranged in a variety of ways for other purposes. For instance, a sampling oscilloscope has been made with a time resolution of 2 psec. But perhaps the best-known application is to computers. Combinations of Josephson junctions can be designed to act as a very fast switch with low power dissipation or as a memory element. The theoretical switching time is about 10 psec and the power dissipation about $1 \mu\text{W}$, giving a product of switching time and power consumption—the figure of merit used for switching devices—several orders of magnitude better than that of transistors. The fabrication of logic elements using such devices allows in principle the construction of a large capacity, compact, high-speed computer [1.20]. Much development work was carried out on this concept during the 1970s, especially by IBM. However, after '15 years and an estimated 100 million dollars' [1.21], IBM announced in 1983 that the project was abandoned, although development work in fact continues at a lower level. During that time, complete logic boards had been developed and tested. Major problems with the technology are that large fan-out ratios are difficult to achieve and that superconducting circuits have a very low inherent impedance and so are difficult to couple with conventional elements at room temperature. There were also manufacturing problems, since the boards could only be tested when in the superconducting state at a low temperature, and some logic gates were always destroyed due to thermal cycling. Another factor was that, as in other branches of superconductivity, room-temperature devices were being developed which approached the advantages offered by the superconducting system; for instance, at the end of 1985, it was reported that miniature ceramic circuit boards and hot electron devices were being developed by Fujitsu of Japan for use in an ambient-temperature computer which would be very much

1. A SUR

faster th
construc
there ha
architect

1.10 Cry

The larg
eering h
and hydr
precooli
carried f
tanks. Th
is at a pr
insulatio
problem:
currents
these pr
small ac
fuel tank

The si
urement:
wavelen
of the ei
supercor
17) is a
utterly n
alternati
then has

1.11 Me

Cryogen
fields. T
been dis
more di
particula
difficult,
processe
by the th
chemical

ations ranging from 10^{-11} T (e brain) [1.19]. Gradiometer o reduce to an acceptably low ie to electrical equipment and he use of ECG and EEG are to the patient, and that the raged over some distance. By or example, brain activity can ion pin-pointed. With a single lays to produce, but attempts using several tens of SQUIDS ed that whereas MRI (Section of tissue, these magnetic field functional behaviour of the etect accumulations of ferro-dy.

i a variety of ways for other pe has been made with a time own application is to comput-in be designed to act as a very as a memory element. The id the power dissipation about and power consumption—the -several orders of magnitude n of logic elements using such of a large capacity, compact, nent work was carried out on BM. However, after '15 years , IBM announced in 1983 that pment work in fact continues : logic boards had been devel- technology are that large fan- perconducting circuits have a ult to couple with conventional also manufacturing problems, n the superconducting state at vere always destroyed due to is in other branches of super- vere being developed which : superconducting system; for that miniature ceramic circuit developed by Fujitsu of Japan er which would be very much

faster than a Josephson machine. However, work continues towards the construction of a complete superconducting computer in Japan, where there have recently been striking advances in fabrication technology and architecture.

1.10 Cryogenics in Space

The large-scale applications of cryogenic technology to aerospace engineering have already been mentioned, in particular the use of liquid oxygen and hydrogen to power launch vehicles, and the use of liquid nitrogen for precooling purposes. In addition, liquid or cold supercritical oxygen is carried for life support, and helium may be carried for pressurising fuel tanks. The technology is similar to that used on earth, except that weight is at a premium, and, once in the space environment, only minimal thermal insulation may be needed. However, the absence of gravity poses serious problems, since liquid no longer separates from vapour and convection currents are non-existent. Special devices have to be used to overcome these problems. In the case of rocket motors, the vehicle may be given a small acceleration by an auxiliary rocket to drive the liquid towards the fuel tank outlet so that the engines may be started reliably.

The small-scale applications are mainly concerned with scientific measurements, including astronomy covering the whole range of electromagnetic wavelengths, recording of magnetic fields and observations of the surface of the earth. The instruments used often include a cooled detector or a superconducting device. The provision of a small refrigerator (see Chapter 17) is attractive, but the device must be of long life (several years), utterly reliable and low in power consumption, weight and vibration. The alternative is to provide a store of cryogenic liquid, but the experiment then has a comparatively short lifetime. Both methods are, in fact, used.

1.11 Medical and Biological Applications

Cryogenics has found a number of applications in the medical and biological fields. The use of superconducting magnets in MRS and MRI has already been discussed, as has the use of SQUIDS. Low temperatures are used more directly to enable biological materials to be frozen and stored, particularly thin tissues and blood. The preservation of large items is more difficult, since the cells suffer damage during the cooling and warming processes, the rapidity of which is inevitably controlled to a great extent by the thermal conductivity of the material, although the injection of certain chemicals can minimise the damage in some cases. On the other hand, this

damage is put to good use in the elimination of tumours by freezing. A major difficulty here lies in the monitoring and control of the frozen region. There is also insufficient understanding of the mechanisms by which cells are killed. Nevertheless, successful results have been obtained in the treatment of some conditions, and it is probable that cryosurgery will be more widely used in the future [1.22].

In agriculture, for many years cattle semen has been routinely preserved in liquid nitrogen for subsequent artificial insemination, and this has made a major contribution to the development of the industry, especially in the underdeveloped countries.

1.12 Cryopumping

Cryopumping—the removal of gas from a system by solidification onto a cold surface—has a number of advantages over other methods of producing vacua. A cryopump consists essentially of a metal plate cooled to a low temperature, and, therefore, can be made easily and economically in a large size, with considerable freedom in design configuration [1.23]. It is a 'clean' pump, since the only working substance is the refrigerant used for cooling, which does not come into contact with the vacuum space. Lastly, all gases except helium can be pumped to extremely low partial pressures (Fig. 1.10).

Although the concept of the cryopump is straightforward, the construction requires some sophisticated design, since the low-temperature parts must be carefully shielded from room-temperature radiation while

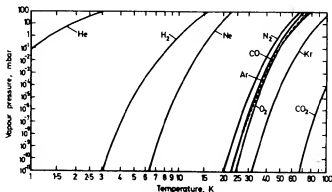


Fig. 1.10 Vapour pressure-temperature curves for atmospheric gases.

Down Lines for
Pneumatics



LN₂ Cooling

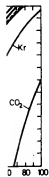


by freezing. A
e frozen region.
s by which cells
obtained in the
surgery will be

tinely preserved
d this has made
specially in the

ification onto a
ds of producing
cooled to a low
onomically in a
on [1.23]. It is a
gerant used for
n space. Lastly,
artial pressures

ward, the con-
w-temperature
radiation while



ic gases.

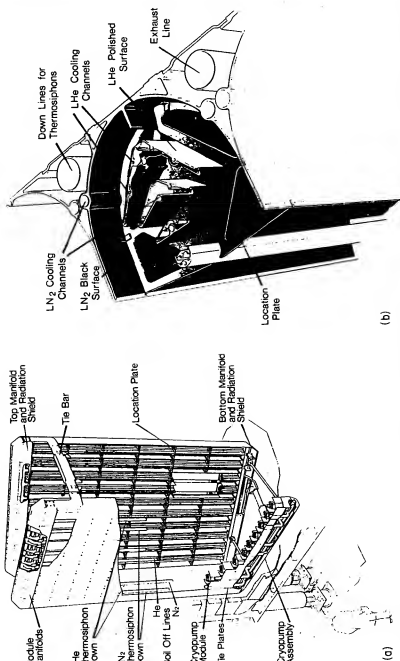


Fig. 1.11 Cryopump designed for the neutral injector assembly of the JET nuclear fusion experiment at Culham, England. The complete assembly is shown in (a). Each module (b) is 0.30×0.35 m in section and 6 m in height. (Courtesy of JET Joint Undertaking.)

allowing free access to gas molecules. This is especially so for cryopumps with stages at 20 K or 4 K, which must be shielded with panels at around 80 K. Since some molecules are scattered away from the cryopumping surface itself by the shields, the overall capture coefficient (which is usually between 0.35 and 0.5 depending on the design) is much less than that of the bare panel and, in fact, is not much different from that of a large diffusion pump.

Very large cryopumps were developed during the 1950s for use in space simulation chambers. Frequently, these used panels cooled to 20 K using a refrigerator with helium gas as the working fluid, and radiation shields cooled either with liquid nitrogen or with helium gas at around 100 K. The residual hydrogen and helium was extracted using conventional high-vacuum pumps. The cryopumps usually covered almost the whole of the interior surface of the vacuum vessel, which typically might be several hundred square metres in area.

Recently, attention has turned to the provision of cryopumps for nuclear fusion experiments. These are required to pump hydrogen at speeds of 10^6 – 10^7 l/sec and to pressures of the order of 10^{-5} mbar or better, so that the coolant must be liquid helium at around 3.5 K. A number of large pumps of this type have now been constructed; advantage has been taken of the geometrical freedom mentioned earlier to produce some interesting configurations [1.24] such as that shown in Fig. 1.11.

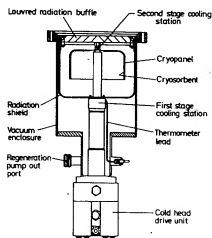


Fig. 1.12 Typical design of a small cryopump attached to a displacer refrigerator and intended to replace a diffusion pump.

At the other cryopumps for be scrupulous apertures of a direct replac contained refr provides refr of course, pur temperature p residual hydrog and zeolites ha low pressures : restricted by a

1.13 Instrumen

The instrumen meter, prol ation. The lat if accurate an procedures, as examined in C

The measure liquids, float g allow the gas temperature of resistors or dio measuring currn in the liquid, a change in heat unreliable beca heat transfer α and a static liqt of the liquid al

In the author hydrostatic hea to room tempel temperature en rising up the m that the liquid

ry cryopumps
s at around
ryopumping
ich is usually
than that of
t of a large

use in space
o 20 K using
tion shields
ound 100 K.
tional high-
whole of the
t be several

s for nuclear
t speeds of
ter, so that
er of large
been taken
interesting

At the other end of the size scale, there is an increasing interest in small cryopumps for industrial purposes, especially where oil contamination must be scrupulously avoided as in the semi-conductor industry. These have apertures of a few tens of centimetres and are frequently designed to be a direct replacement for a diffusion pump. They are cooled with a small self-contained refrigerator based on a displacer cycle (see Chapter 17) which provides refrigeration at around 100 K for the radiation shield (which also, of course, pumps water vapour), and cooling at around 20 K for the lower temperature panel, which is equipped with a sorbent material to pump residual hydrogen (Fig. 1.12). Sorbent materials such as activated charcoal and zeolites have attracted attention on account of their ability to achieve low pressures at comparatively high temperatures. However, their use is restricted by a low pumping speed and a limited absorption capacity.

1.13 Instrumentation

The instrument most commonly used in cryogenic engineering is the thermometer, probably on account of its cheapness and simplicity of installation. The latter is deceptive, however, and great care must be taken if accurate and reliable measurements are to be obtained. Installation procedures, as well as the many different types of sensor available, are examined in Chapter 18.

The measurement of liquid level can present problems. For the denser liquids, float gauges can be used, provided that the float is designed to allow the gas inside to contract or even condense, depending on the temperature of the liquid. A popular electronic device is a chain of carbon resistors or diodes which essentially act as resistance thermometers. The measuring current is adjusted so that when the sensor ceases to be immersed in the liquid, a large temperature change of the sensor occurs due to the change in heat transfer coefficient. However, the method tends to be unreliable because the current must be carefully adjusted and because the heat transfer coefficient can be similar in a fast-flowing stream of vapour and a static liquid. Difficulties can also arise if the saturation temperature of the liquid alters due to a change in pressure.

In the author's view, the most reliable method is simply to measure the hydrostatic head of liquid, using pressure tappings which are brought up to room temperature to a suitable differential pressure gauge. At the low-temperature end, to eliminate hydrostatic head errors due to the liquid rising up the measuring tube, the tube must be arranged horizontally so that the liquid boils in the horizontal portion. Boiling can be ensured by

using a small heater if the natural heat leak from room temperature is not sufficient. Errors may occur because of unknown temperature gradients in the liquid and also in the vapour, whose density is often not negligible compared with that of the liquid, especially in helium systems.

For liquid helium in the absence of strong magnetic fields, the superconducting gauge is undoubtedly the most convenient and accurate, measuring level to within a few millimetres. The sensor consists of a length of Type II superconducting wire, which is heated so that it is superconducting below the liquid level, but normal above, so that the resistance is just proportional to the length of wire above the free surface. The state of the wire when in the vapour will again depend on the local heat transfer coefficient, but nevertheless a well-designed sensor appears to be unaffected by high velocity flows of cold gas. The heater is sometimes separate from the wire, sometimes the measuring current itself is sufficient.

Many types of flowmeter have been used at cryogenic temperatures, with varied success, although it is usual to measure the flow at room temperature if possible. The low viscosity of the liquids, and their low density, means that turbine meters are not responsive to changes in flow rate, and also may be damaged by overspeeding due to the large gas flows during cooldown of the system; a bypass may therefore be necessary. If the liquid is near saturation, vapour may be formed in the throats of orifice plates and venturi meters unless the pressure differential is so low that it is difficult to measure. Again, the measuring equipment may be damaged during cooldown because of the large pressure differentials which may be developed. Ultrasonics and thermal anemometry have been used with some success, but the equipment is expensive and difficult to install in a cryogenic environment. Except for very small pipelines, the vortex-shedding meter may be the best type to use.

A wide range of other instruments has been used in a cryogenic environment. Generally, instruments used for room-temperature applications can be adapted, with a careful choice of materials, unless the measuring phenomenon itself is very sensitive to temperature or does not exist in the cryogenic temperature range. Many types of transistors will operate satisfactorily right down to liquid helium temperatures [1.16, 1.25], and this fact has been exploited in the design of many instruments.

References

- 1.1 N. Kurti, 'Low Temperature Terminology', *Proc. XIII Int. Congr. Refrig.*, Vol. 1, pp. 593-597 (Int. Inst. Refrig., 1973).
1. A SURVEY
- 1.2 N. Kurti, "
- 1.3 Data kindly
- 1.4 E. K. Farid: *Gastech* 81, 1982).
- 1.5 A. O. Tisel 1-10 (1966)
- 1.6 E. F. Hamr (1980); A. J there a crisis
- 1.7 C. H. Rode *Cryog. Eng.*
- 1.8 L. J. Neuri pp. 32-43, 1 'Supercondi 53.
- 1.9 B. J. Maddk *Cryog. Eng.* conducting: 598, Genov:
- 1.10 B. C. Belan in the U.S. (1975).
- 1.11 E. B. Forsyt *Cryogenics* 1
- 1.12 *Cryogenics*:
- 1.13 R. I. Schen storage syst 123-132 (19
- 1.14 T. Ohtsuka in Japan', (1984).
- 1.15 J. H. P. Wat presented at
- 1.16 R. K. Kirsed
- 1.17 H. M. Rose
- 1.18 T. van Duz Edward Arn
- 1.19 S. J. William 22, 129-201
- 1.20 J. Matisoo, 1980).
- 1.21 *The Times*:
- 1.22 P. Le Pivert *Engng Conf.*
- 1.23 B. A. Hand
- 1.24 B. A. Hand
- 1.25 B. Lengeler, *genics* 14, 43

1. A SURVEY OF CRYOGENIC ENGINEERING

- 1.2 N. Kurti, 'From Caillietet and Pictet to microkelvin', *Cryogenics* **18**, 451-458 (1978).
- 1.3 Data kindly supplied by R. M. Thorogood.
- 1.4 E. K. Faridany, 'International trade in LNG: present projects and future outlook', *Proc. Gastech 81 LNG/LPG Conference*, pp. 21-35 (Gastech Ltd., Rickmansworth, England, 1982).
- 1.5 A. O. Tischler, 'The impact of the space age on cryogenics', *Adv. Cryog. Engng* **11**, 1-10 (1966).
- 1.6 E. F. Hammel, 'Helium: its past, present and future', *Adv. Cryog. Engng* **25**, 810-821 (1980); A. Francis, D. Keierleber and D. Swartz, 'Helium prospects for the future: is there a crisis?', *Adv. Cryog. Engng* **29**, 9-17 (1984).
- 1.7 C. H. Rode, 'Cryogenic system for a 100 km superconducting collider', *Proc. 10th Int. Cryog. Engng Conf.*, pp. 760-770, Helsinki, Finland (1984).
- 1.8 L. J. Neuringer, 'NMR in biology and medicine', *Proc. 10th Int. Cryog. Engng Conf.*, pp. 32-43, Helsinki, Finland (1984); M. F. Wood, I. L. MacDougall and P. H. Winson, 'Superconducting magnets for NMR imaging and in-vivo spectroscopy', *ibid.*, pp. 44-53.
- 1.9 B. J. Maddock and W. T. Norris, 'Superconductivity in electricity supply', *Proc. 7th Int. Cryog. Engng Conf.*, pp. 245-259, London, England (1978); J. G. Steel, 'Superconducting a.c. generators - a utility view', *Proc. 8th Int. Cryog. Engng Conf.*, pp. 590-598, Genova, Italy (1980).
- 1.10 B. C. Belanger, 'Superconducting and resistive cryogenic power transmission research in the U.S. - an opportunity for cryogenic innovation', *Adv. Cryog. Engng* **20**, 1-22 (1975).
- 1.11 E. B. Forsyth, 'Cryogenic engineering for the Brookhaven power transmission project', *Cryogenics* **17**, 3-7 (1977).
- 1.12 *Cryogenics* **25**, 50 (1985).
- 1.13 R. I. Schermer *et al.*, 'Design and operation of the 30 MJ superconducting magnetic storage system on the Bonneville Power Administration bus', *Adv. Cryog. Engng* **29**, 123-132 (1984).
- 1.14 T. Ohtsuka and Y. Kyotani, 'Recent progress on superconducting magnetic levitation in Japan', *Proc. 10th Int. Cryog. Engng Conf.*, pp. 750-759, Helsinki, Finland (1984).
- 1.15 J. H. P. Watson, 'Status report on magnetic separation using superconducting magnets', presented at 10th Int. Cryog. Engng Conf., Helsinki, Finland (1984).
- 1.16 R. K. Kirschman, 'Cold electronics: an overview', *Cryogenics* **25**, 115-122 (1985).
- 1.17 H. M. Rosenberg, *The Solid State*, 2nd edn, Clarendon Press (1978).
- 1.18 T. van Duzer and C. W. Turner, *Principles of Superconductive Devices and Circuits*, Edward Arnold (1981).
- 1.19 S. J. Williamson and L. Kaufman, 'Biomagnetism', *J. Magnetism and Magn. Materials* **22**, 129-201 (1981).
- 1.20 J. Matsoo, 'The superconducting computer', *Scientific American* **282** (5), 38-53 (May 1980).
- 1.21 *The Times*, London, 1 December 1983, p. 19.
- 1.22 P. Le Pivert, 'Cryosurgery: current issues and future trends', *Proc. 10th Int. Cryog. Engng Conf.*, pp. 551-557, Helsinki, Finland (1984).
- 1.23 B. A. Hands, 'Introduction to cryopump design', *Vacuum* **26**, 11-16 (1976).
- 1.24 B. A. Hands, 'Recent developments in cryopumping', *Vacuum* **32**, 603-612 (1982).
- 1.25 B. Lengeler, 'Semiconductor devices suitable for use in cryogenic environments', *Cryogenics* **14**, 439-447 (1974).

Journals

The most useful regular cryogenic publications are:

Cryogenics, a journal published by Butterworth Scientific Ltd., Guildford, England.
Advances in Cryogenic Engineering, which is published by Plenum Press and is the proceedings of the biennial Cryogenic Engineering Conference and the concurrent International Cryogenic Materials Conference held in the USA. It is referred to in this volume as *Adv. Cryog. Engng.*

Proceedings of the International Cryogenic Engineering Conference series (ICEC), published by Butterworth Scientific Ltd., Guildford, England, and predecessors.

Proceedings of the LNG and GasTech Conferences, which contain information on developments in LNG technology.

IC SQUID, proceedings of the International Conferences on SQUIDS.

International Institute of Refrigeration (IIR) conference proceedings.

Proceedings of the Applied Superconductivity Conference series.

General Bibliography

In reverse order of publication:

- R. F. Barron, *Cryogenic Systems*, 2nd edn, Oxford University Press (1985).
- K. D. Williamson, Jr. and F. J. Edeskuty (eds), *Liquid Cryogenics Vol. 1: Theory and Equipment*; Vol. 2: *Properties and Applications*, CRC Press (1983).
- A. Arkharov, I. Marfenina and Ye. Mikulin, *Theory and Design of Cryogenic Systems*, MIR Publishers (1981).
- G. K. White, *Experimental Techniques in Low-Temperature Physics*, 3rd edn, Clarendon Press (1979).
- A. C. Rose-Innes, *Low Temperature Laboratory Techniques. The Use of Liquid Helium in the Laboratory*, 2nd edn, English Universities Press (1973).
- C. A. Bailey (ed.), *Advanced Cryogenics*, Plenum Press (1971).
- G. G. Haselden (ed.), *Cryogenic Fundamentals*, Academic Press (1971).
- H. Weinstock (ed.), *Cryogenic Technology*, Boston Tech. Publ. (1969).
- R. H. Kropschot, B. W. Birmingham and D. B. Mann (eds), *Technology of Liquid Helium*, NBS Monograph 111 (1968).
- R. B. Scott, W. H. Denton and C. M. Nicholls (eds), *Technology and Uses of Liquid Hydrogen*, Pergamon Press (1964).
- J. H. Bell, *Cryogenic Engineering*, Prentice Hall (1963).
- R. W. Vance (ed.), *Cryogenic Technology*, John Wiley (1963).
- R. W. Vance and W. M. Duke (eds), *Applied Cryogenic Engineering*, John Wiley (1962).
- R. B. Scott, *Cryogenic Engineering*, Van Nostrand (1959).

Bibliography of Specific Topics

In alphabetical order of author:

- A. Barone and G. Paternò, *Physics and Applications of the Josephson Effect*, Wiley-Interscience (1982).
- N. R. Braton, *Cryogenic Recycling and Processing*, CRC Press (1980).

I. A. St

British

Mech

J. R. B

A. J. C

B. Dea

T. van I

Arno

R. C. I

Press

D. Fish

S. Fone

Appl

R. A. F

(Engl

H. von

W. L. I

W. R. I

Topic

M. Rec

A. C. R

Press

R. P. S

B. B. S

Plenu

F. H. T

M. N. 1

Non-sj

K. Men

Weid

D. Wil

(1979

- British Cryogenics Council, *Cryogenics Safety Manual - A Guide to Good Practice*, 2nd edn, Mechanical Engineering Publications, Bury St. Edmunds (1982).
- J. R. Bumby, *Superconducting Rotating Electrical Machines*, Clarendon Press (1983).
- A. J. Croft, *Cryogenic Laboratory Equipment*, Plenum Press (1970).
- B. Deaver and J. Ruvalds (eds), *Advances in Superconductivity*, Plenum Press (1983).
- T. van Duzer and C. W. Turner, *Principles of Superconductive Devices and Circuits*, Edward Arnold (1981).
- R. C. Flook, *Natural Gas by Sea*, Gentry Books, London (1979); *Gas Carriers*, Fairplay Press, London (1984).
- D. Fishlock (ed.), *A Guide to Superconductivity*, Macdonald-Elsevier (1969).
- S. Foner and B. B. Schwartz (eds), *Superconducting Machines and Devices - Large Systems Applications*, Plenum Press (1974).
- R. A. Haefer, *Kryo-Vakuumtechnik: Grundlagen und Anwendungen*, Springer-Verlag (1981) (English translation to be published by Oxford University Press).
- H. von Leden and W. G. Cahan, *Cryogenics in Surgery*, H. K. Lewis (1971).
- W. L. Lom, *Liquefied Natural Gas*, Applied Science Publishers (1974).
- W. R. Parrish, R. O. Voth, J. G. Hust, T. M. Flynn, C. F. Sindt and N. A. Olien, *Selected Topics on Hydrogen Fuel*, NBS Special Publication 419 (1975).
- M. Rechowicz, *Electric Power at Low Temperatures*, Clarendon Press (1975).
- A. C. Rose-Innes and E. H. Rhoderick, *Introduction to Superconductivity*, 2nd ed., Pergamon Press (1978).
- R. P. Shutt (ed.), *Bubble and Spark Chambers, Vol. 1*, Academic Press (1967).
- B. B. Schwartz and S. Foner (eds), *Superconductor Applications: SQUIDS and Machines*, Plenum Press (1977).
- F. H. Turner, *Concrete and Cryogenics*, Cement and Concrete Ass., England (1979).
- M. N. Wilson, *Superconducting Magnets*, Clarendon Press (1983).

Non-specialist Reading

- K. Mendelssohn, *The Quest for Absolute Zero; the Meaning of Low Temperature Physics*, Weidenfeld & Nicholson (1966).
- D. Wilson, *Supercold, an Introduction to Low Temperature Technology*, Faber & Faber (1979).

(1985).
s Vol. 1: *Theory and*
ryogenic Systems, MIR

s, 3rd edn, Clarendon
se of Liquid Helium in

71).
9).
logy of Liquid Helium,

y and Uses of Liquid

g, John Wiley (1962).

sephson Effect, Wiley-

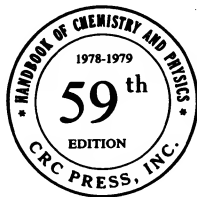
0).

ATTACHMENT B

VCE
tion
ogy,
VCE

CRC Handbook OF Chemistry and Physics

A Ready-Reference Book of Chemical and Physical Data



EDITOR

ROBERT C. WEAST, Ph.D.

*Vice President, Research, Consolidated Natural Gas Service Company, Inc.
Formerly Professor of Chemistry at Case Institute of Technology*

ASSOCIATE EDITOR

MELVIN J. ASTLE, Ph.D.

*Formerly Professor of Organic Chemistry at Case Institute of Technology
and
Manager of Research at Glidden-Durkee Division of SCM Corporation*

SES

In collaboration with a large number of professional chemists and physicists whose assistance is acknowledged in the list of general collaborators and in connection with the particular tables or sections involved.



CRC PRESS, Inc.
2255 Palm Beach Lakes Blvd., West Palm Beach, Florida 33409

Superconductivity*

B.W. ROBERTS

General Electric Research Laboratory, Schenectady, New York

The following tables on superconductivity include superconductive properties of chemical elements, thin films, a selected list of compounds and alloys, and high-magnetic-field superconductors.

The historically first observed and most distinctive property of a superconductive body is the near total loss of resistance at a critical temperature (T_c) that is characteristic of each material. Figure 1(a) below illustrates schematically two types of possible transitions. The sharp vertical discontinuity in resistance is indicative of that found for a single crystal of a very pure element or one of a few well annealed alloy compositions. The broad transition, illustrated by broken lines, suggests the transition shape seen for materials that are not homogeneous and contain unusual strain distributions. Careful testing of the resistivity limits for superconductors shows that it is less than 4×10^{-23} ohm-cm, while the lowest resistivity observed in metals is of the order of 10^{-13} ohm-cm. If one compares the resistivity of a superconductive body to that of copper at room temperature, the superconductive body is at least 10^{17} times less resistive.

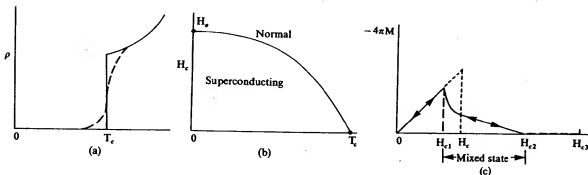


Figure 1. PHYSICAL PROPERTIES OF SUPERCONDUCTORS

- (a) Resistivity versus temperature for a pure and perfect lattice (solid line). Impure and/or imperfect lattice (broken line).
- (b) Magnetic-field temperature dependence for Type-I or "soft" superconductors.
- (c) Schematic magnetization curve for "hard" or Type-II superconductors.

The temperature interval ΔT_c , over which the transition between the normal and superconductive states takes place, may be of the order of as little as 2×10^{-5} °K or several °K in width, depending on the material state. The narrow transition width was attained in 99.9999 percent pure gallium single crystals.

A Type-I superconductor below T_c , as exemplified by a pure metal, exhibits perfect diamagnetism and excludes a magnetic field up to some critical field H_c , whereupon it reverts to the normal state as shown in the H-T diagram of Figure 1(b).

The difference in entropy near absolute zero between the superconductive and normal states relates directly to the electronic specific heat, γ : $(S_n - S_s)_{T \rightarrow 0} = -\gamma T$.

The magnetization of a typical high-field superconductor is shown in Figure 1(c). The discovery of the large current-carrying capability of Nb_3Sn and other similar alloys has led to an extensive study of the physical properties of these alloys. In brief, a high-field superconductor, or Type-II superconductor, passes from the perfect diamagnetic state at low magnetic fields to a mixed state and finally to a sheathed state before attaining the normal resistive state of the metal. The magnetic field values separating the four stages are given as H_{c1} , H_{c2} , and H_{c3} . The superconductive state below H_{c1} is perfectly diamagnetic, identical to the state of most pure metals of the "soft" or Type-I

*Prepared for Office of Standard Reference Data, National Bureau of Standards, by Standard Reference Data Center on Superconductive Materials, Schenectady, N.Y.

superconductor. Between H_{c1} and H_{c2} a "mixed superconductive state" is found in which fluxons (a minimal unit of magnetic flux) create lines of normal superconductor in a superconductive matrix. The volume of the normal state is proportional to $-4\pi M$ in the "mixed state" region. Thus at H_{c2} the fluxon density has become so great as to drive the interior volume of the superconductive body completely normal. Between H_{c2} and H_{c3} the superconductor has a sheath of current-carrying superconductive material at the body surface, and above H_{c3} the normal state exists. With several types of careful measurement, it is possible to determine H_{c1} , H_{c2} , and H_{c3} . Table 2-35 contains some of the available data on high-field superconductive materials.

High-field superconductive phenomena are also related to specimen dimension and configuration. For example, the Type-I superconductor, Hg, has entirely different magnetization behavior in high magnetic fields when contained in the very fine sets of filamentary tunnels found in an unprocessed Vycor glass. The great majority of superconductive materials are Type II. The elements in very pure form and a very few precisely stoichiometric and well annealed compounds are Type-I with the possible exceptions of vanadium and niobium.

Metallurgical Aspects. The sensitivity of superconductive properties to the material state is most pronounced and has been used in a reverse sense to study and specify the detailed state of alloys. The mechanical state, the homogeneity, and the presence of impurity atoms and other electron-scattering centers are all capable of controlling the critical temperature and the current-carrying capabilities in high-magnetic fields. Well annealed specimens tend to show sharper transitions than those that are strained or inhomogeneous. This sensitivity to mechanical state underlines a general problem in the tabulation of properties for superconductive materials. The occasional divergent values of the critical temperature and of the critical fields quoted for a Type-II superconductor may lie in the variation in sample preparation. Critical temperatures of materials studied early in the history of superconductivity must be evaluated in light of the probable metallurgical state of the material, as well as the availability of less pure starting elements. It has been noted that recent work has given extended consideration to the metallurgical aspects of sample preparation.

REFERENCES

References to the data presented in this section, to additional entries of superconductive materials, and to those materials specifically tested and found non-superconductive to some low temperature may be found in the following publications:

- "Superconductive Materials and Some of Their Properties", *Progress in Cryogenics*, B.W. Roberts, Vol. IV, Heywood and Co., 1964, pp. 160-231.
- "Superconductive Materials and Some of Their Properties", B.W. Roberts, National Bureau of Standards Technical Notes 408 and 482, U.S. Government Printing Office, 1966 and 1969.

SELECTED PROPERTIES OF THE SUPERCONDUCTIVE ELEMENTS

Conversion Factors

$$\text{Oe} \times 79.57 = \text{A/m}; \text{katm} \times 1.013 \times 10^4 = \text{N/m}^2; \text{kb} \times 1.0 \times 10^4 = \text{N/m}^2$$

Element	$T_c(\text{K})$	$H_c(\text{oersteds})$	$\theta_D(\text{K})$	$\gamma(\text{mJmole}^{-1} \text{deg} \cdot \text{K}^2)$
Al	1.175	104.93	420	1.35
Be	0.026			0.21
Cd	0.518, 0.52	29.6	209	0.688
Ga	1.0833	59.3	325	0.60
Ga (β)	5.90, 6.2	560		
Ga (γ)	7.62	950		
Ga (δ)	7.85	815		
Hg (α)	4.154	411	87, 71.9	1.81
Hg (β)	3.949	339	93	1.37
In	3.405	281.53	109	1.672
Ir	0.14, 0.11	19	425	3.27
La (α)	4.88	808, 798	142	10.0, 11.3
La (β)	6.00	1,096	139	11.3
Mo	0.916	90, 98	460	1.83
Nb	9.25	1,970	277, 238	7.80
Os	0.655	65	500	2.35
Pa	1.4			
Pb	7.23	803	96.3	3.0
Re	1.697	188, 211	415	2.35
Ru	0.493	66	580	3.0
Sb	2.6-2.7			
Sn	3.721	305	195	1.78
Ta	4.47	831	258	6.15
Tc	7.73, 7.78	1,410	411	4.84, 6.28
Th	1.39	159.1	165	4.31
Ti	0.39	56, 100	429, 412	3.32
Tl	2.332, 2.39	181	78.5	1.47
V	5.43, 5.31	1,100, 1,400	382	9.82
W	0.0154	1.15	550	0.90
Zn	0.875	55	319.7	0.633
Zr	0.53	47	290	2.78
Zr (ω)	0.65			

Thin Films Condensed at Various Temperatures

Element	$T_c(\text{K})$
Al	1.18-5.7
Be	-03, -9.6; 6.5-10.6 ^a ; 10.2 ^b
Bi	-2-5, 6.11, 6.154, 6.173
Cd	0.53-0.91
Ga	6.4-6.8, 7.4-8.4, 8.56
In	3.43-4.5; 3.68-4.17 ^c
La	5.0-6.74
Mo	3.3-3.8, 4-6.7
Nb	6.2-10.1
Pb	-2-7.7
Re	-7
Sn	3.6, 3.84-6.0
Ta	<1.7-4.25, 3.16-4.8
Ti	1.3
Tl	2.64
V	5.14-6.02
W	<1.0-4.1
Zn	0.77-1.48

^aWith KCl.

^bWith Zn etioporphyrin.

^cIn glass pores.

SELECTED PROPERTIES OF THE SUPERCONDUCTIVE ELEMENTS (Continued)

Data for Elements Studied Under Pressure

Element	$T_c(K)$	Pressure
As	0.31-0.5	220-140 kb
	0.2-0.25	~140-100 kb
Ba II	~1.3	55 kb
Ba III	3.05	85-88 kb
	~5.2	>140 kb
Bi II	3.916	25 katm
	3.90	25.2 katm
	3.86	26.8 katm
Bi III	6.55	~37 kb
	7.25	27-28.4 katm
Bi IV	7.0	43, 43-62 kb
Bi V	8.3, 8.55	81 kb
Bi VI	8.55	90, 92-101 kb
Ce	1.7	50 kb
Cs	~1.5	>~125 kb
Ga II	6.24, 6.38	>35 katm
Ga II'	7.5	>35 katm ($P \rightarrow 0$)
Ge	4.85-5.4	~120 kb
	5.35	115 kb
La	~5.5-11.93	0-~140 kb
P	4.7	>100 kb
	5.8	170 kb
Pb II	3.55, 3.6	160 kb
Sb	3.55	85 kb
	3.52	93 kb
	3.53	100 kb
	3.40	~150 kb
Se II	6.75, 6.95	~130 kb
Si	6.7, 7.1	120 kb
Sn II	5.2	125 kb
	4.85	160 kb
Sn III	5.30	113 kb
Te II	2.05	43 kb
	3.4	50 kb
Te III	4.28	70 kb
Te IV	4.25	84 kb
Tl, cub.	1.45	35 kb
Tl, hex.	1.95	35 kb
U	2.3	10 kb
Y	~1.2, ~2.7	120-170 kb

From Roberts, B. W., Properties of Selected Superconductive Materials, 1974 Supplement, NBS Technical Note 825, U.S. Government Printing Office, Washington, D.C., 1974, 10.

All compositions are denoted on an atomic basis, i.e., AB, AB₂, or AB₃ for compounds, unless noted. Solid solutions or odd compositions may be denoted as A_xB_{1-x} or A_xB. A series of three or more alloys is indicated as A_xB_{1-x} or by actual indication of the atomic fraction range, such as A_{0-0.6}B_{1-0.4}. The critical temperature of such a series of alloys is denoted by a range of values or possibly the maximum value.

The selection of the critical temperature from a transition in the effective permeability, or the change in resistance, or possibly the incremental changes in frequency observed by certain techniques is not often obvious from the literature. Most authors choose the mid-point of such curves as the probable critical temperature of the idealized material, while others will choose the highest temperature at which a deviation from the normal state property is observed. In view of the previous discussion concerning the variability of the superconductive properties as a function of purity and other metallurgical aspects, it is recommended that appropriate literature be checked to determine the most probable critical temperature or critical field of a given alloy.

A very limited amount of data on critical fields, H_c , is available for these compounds and alloys; these values are given at the end of the table.

SYMBOLS: n = number of normal carriers per cubic centimeter for semiconductor superconductors.

Substance	T_c , °K	Crystal structure type††	Substance	T_c , °K	Crystal structure type††
Ag ₈ Al ₂ Zn _{1-x-y}	0.5-0.845	Cubic	Al _{1-0.8} Ge _{0.2} Nb ₃	20.7	A15
Ag ₂ BF ₄ O ₈	0.15		AlLa ₃	5.57	DO ₁₉
AgBi ₂	3.0-2.78		Al ₂ La	3.23	C15
Ag ₇ F _{0.25} N _{0.75} O _{10.25}	0.85-0.90	Cubic	Al ₃ Mg ₂	0.84	Cubic, f.c.
Ag ₅ FO ₈	0.3		AlMo ₃	0.58	A15
Ag ₂ F	0.066		AlMo ₆ Pd	2.1	
Ag _{0.8-0.3} Ga _{0.2-0.7}	6.5-8	Hex., c.p.	AlN	1.55	B4
Ag ₆ Ge	0.85		Al ₂ NNb ₃	1.3	Al3
Ag _{0.438} Hg _{0.562}	0.64		AlNb ₃	18.0	A15
AgIn ₂	~2.4	C16	Al ₂ Nb _{1-x}	<4.2-13.5	D8 _h
Ag _{0.1} In _{0.9} Te (n = 1.40 × 10 ²²)	1.20-1.89	BI	Al ₂ Nb _{1-x}	12-17.5	A15
Ag _{0.2} In _{0.8} Te (n = 1.07 × 10 ²²)	0.77-1.00	BI	Al _{0.27} Nb _{0.73-0.48} VO _{0-0.25}	14.5-17.5	A15
AgLa (9.5 kbar)	1.2	B2	AlNb ₃ V _{1-x}	<4.2-13.5	
Ag ₃ NO ₁₁	1.04	Cubic	AlOs	0.39	B2
Ag ₃ Pb _{1-x}	7.2 max.		Al ₃ Os	5.90	
Ag ₃ Sn _{1-x} (film)	2.0-3.8		AlPb (films)	1.2-7	
Ag ₃ Sn _{1-x}	1.5-3.7	Cubic	Al ₂ Pt	0.48-0.55	C1
AgTe ₃	2.6		Al ₃ Re ₂₄	3.35	Al2
AgTh ₂	2.26		Al ₃ Th	0.75	DO ₁₉
Ag _{0.03} Tl _{0.97}	2.67	C16	Al ₂ Ti ₂ V _{1-x-y}	2.05-3.62	Cubic
Ag _{0.94} Tl _{0.06}	2.32		Al _{0.108} VO _{0.892}	1.82	Cubic
Ag ₂ Zn _{1-x}	0.5-0.845		Al ₂ Zn _{1-x}	0.5-0.845	
Al (film)	1.3-2.31	Al	AlZr ₃	0.73	LI ₂
Al (1 to 21 atm)	1.170-0.687		AsBiPb	9.0	
AlAu ₄	0.4-0.7		AsBiPbSb	9.0	
Al ₂ CMo ₃	10.0	Al3 + trace 2nd phase	As _{0.33} InTe _{0.67} (n = 1.24 × 10 ²²)	0.85-1.15	BI
Al ₂ CMo ₃	9.8-10.2		As _{0.2} InTe _{0.8} (n = 0.97 × 10 ²²)	0.44-0.62	BI
Al ₂ CaSi	5.8		As _{0.30} Ni _{0.06} Pd _{0.64}	1.39	C2
Al _{0.131} Cr _{0.088} VO _{0.781}	1.46	Cubic	AsPb	8.4	
AlGe ₂	1.75		AsPd ₂ (low- temperature phase)	0.60	Hexagonal
Al _{0.5} Ge _{0.3} Nb	12.6	A15	AsPd ₂ (high-temp. phase)	1.70	C22

††See key at end of table.

SELECTED SUPERCONDUCTIVE COMPOUNDS AND ALLOYS (Continued)

Substance	T_c , °K	Crystal structure type††	Substance	T_c , °K	Crystal structure type††
AsPd ₃	0.46	Complex	BW ₂	3.1	Cl6
AsRh	0.58	B31	B ₂ Y	6.5-7.1	
AsRh _{1.4-1.6}	<0.03-0.56	Hexagonal	B ₁₂ Y	4.7	
AsSn	4.10		BZr	3.4	Cubic
AsSn			B ₁₂ Zr	5.82	
($n = 2.14 \times 10^{22}$)	3.41-3.65	BI	BaBi ₃	5.69	Tetragonal
As _{0.25} Sn _{0.3}	3.5-3.6, 1.21-1.17		Ba _{0.75} O ₇ Sr _{1.25} Ti ($n = 4.2-11 \times 10^{19}$)	<0.1-0.55	
As ₂ Sn ₄ ($n = 0.56 \times 10^{22}$)	1.16-1.19	Rhombohedral	Ba _{0.13} O ₃ W	1.9	Tetragonal
Au ₂ Ba	0.4-0.7	D _{2d}	Ba _{0.14} O ₃ W	<1.25-2.2	Hexagonal
AuBe	2.64	B20	BaRh ₂	6.0	Cl5
Au ₂ Bi	1.80	Cl5	Be ₂₂ Mo	2.51	Cubic, like Be ₂₂ Re
Au ₂ Ca	0.34-0.38	Cl5 ₂	Be ₂ Nb ₂ Zr ₂	5.2	
AuGa	1.2	B31	Be _{0.98-0.93} Re _{0.02-0.08} (quenched)	9.5-9.75	Cubic
Au _{0.40-0.92} Ge _{0.60-0.08}	<0.32-1.63	Complex	Be _{0.95} Re _{0.05}	9.62	Cubic, like Be ₂₂ Re
AuIn	0.4-0.6	Complex	BeTe	5.21	Cubic
AuLu	<0.35	B2	Be ₂₂ W	4.12	Cubic, like Be ₂₂ Re
AuNb ₃	11.5	A15	Be ₁₃ W	4.1	Tetragonal
AuNb ₃	1.2	A2	Bi ₂ Ca	2.0	
Au _{0-0.3} Nb _{1-0.7}	1.1-11.0	A15	Bi _{0.5} Cd _{0.13} Pb _{0.25} Sn _{0.12} (weight fractions)	8.2	
Au _{0.02-0.98} Nb _{0.98-0.02}	2.53-10.9	A15	BiCo	0.42-0.49	Cl5
AuNb _{3(1-x)} V _{3x}	1.5-11.0		Bi ₂ Cs	4.75	
AuPb ₂	3.15		Bi ₂ Cu _{1-x} (electrodeposited)	2.2	
AuPb ₂ (film)	4.3	Cl5	Bi _{0.019} In _{0.981}	1.33-1.40	
AuPb ₃	4.40	C2	Bi _{0.05} In _{0.95}	4.65	α -phase
AuPb ₃ (film)	4.25	B8 ₁	Bi _{0.10} In _{0.90}	5.05	α -phase
Au ₂ Pb	1.18, 6-7		Bi _{0.15-0.30} In _{0.85-0.70}	5.3-5.4	α - and β -phases
AuSb ₂	0.58		Bi _{0.34-0.48} In _{0.66-0.52}	4.0-4.1	
AuSn	1.25		Bi ₂ In ₃	4.1	β -phase
Au ₂ Sn _{1-x} (film)	2.0-3.8	A3	BiIn ₂	5.65	
Au ₂ Sn	0.7-1.1	Cubic	Bi ₂ Ir	1.7-2.3	
Au ₂ Tc ₃	1.62	Cl6	Bi ₂ Ir (quenched)	3.0-3.96	
AuTb ₃	3.08		BiK	3.6	
AuTi	1.92	A15	Bi ₂ K	3.58	Cl5
AuV ₃	0.74		BiLi	2.47	Li ₀ , α -phase
Au ₂ Zn _{1-x}	0.50-0.845	Cubic	Bi _{1-0.9} Mg	0.7-~1.0	
Au ₂ Zr ₃	1.21	A3	Bi ₃ Mo	3-3.7	
Au ₂ Zr ₃	1.7-2.8	A15	BiNa	2.25	Li ₀
AuZr ₃	0.92	Orthorhombic	BiNb ₃ (high pressure and temperature)	3.05	A15
BCMo ₂	5.4		BiNi	4.25	B8 ₁
BCMo ₂	12.5		Bi ₂ Ni	4.06	Orthorhombic
B _{0.03} C _{0.97} Mo _{0.47}	5.3-7.0	Orthorhombic	Bi ₁₋₀ Pb ₀₋₁	7.26-9.14	
BHF	3.1	Cubic	Bi ₁₋₀ Pb ₀₋₁ (film)	7.25-8.67	
B ₆ La	5.7		Bi _{0.05-0.40} Pb _{0.95-0.60}	7.35-8.4	Hexagonal, c.p., to ϵ -phase
B ₁₂ Lu	0.48				
BMo	0.5 (extrapolated)				
BMo ₂	4.74	Cl6			
BNb	8.25	B ₇			
BRe ₂	2.80, 4.6				
B _{0.3} Ru _{0.7}	2.58	D10 ₂			
B ₁₂ Sc	0.39				
BTa	4.0	B ₇			
B ₆ Th	0.74		BiPbSb	8.9	

†† See key at end of table.

SELECTED SUPERCONDUCTIVE COMPOUNDS AND ALLOYS (Continued)

	Substance	T_c , °K	Crystal structure type††	Substance	T_c , °K	Crystal structure type††
	$\text{Bi}_{0.3}\text{Pb}_{0.31}\text{Sn}_{0.19}$ (weight fractions)	8.5		$\text{Co}_{0.44}\text{Mo}_{0.56}$	1.3	BI
	$\text{Bi}_{0.3}\text{Pb}_{0.23}\text{Sn}_{0.23}$	8.5		$\text{Co}_{0.3}\text{Mo}_{0.7}\text{Nb}_{1-x}$	10.8–12.5	BI
	BiPd_2	4.0		$\text{Co}_{0.4}\text{Mo}_{0.6}\text{Si}_3$	7.6	D8 ₈
al	$\text{Bi}_{0.4}\text{Pd}_{0.6}$	3.7–4	Hexagonal, ordered	$\text{CMo}_{0.2}\text{Ta}_{0.8}$	7.5	BI
	BiPd	3.7	Orthorhombic	$\text{CMo}_{0.5}\text{Ta}_{0.5}$	7.7	BI
al	Bi_2Pd	1.70	Monoclinic, α -phase	$\text{CMo}_{0.75}\text{Ta}_{0.25}$	8.5	BI
al	Bi_2Pd	4.25	Tetragonal, β -phase	$\text{CMo}_{0.8}\text{Ta}_{0.2}$	8.7	BI
				$\text{CMo}_{0.81}\text{Ta}_{0.19}$	8.9	BI
				$\text{CMo}_2\text{Ti}_{1-x}$	10.2 max.	BI
				$\text{CMo}_{0.81}\text{Ti}_{0.19}$	10.2	BI
				$\text{CMo}_2\text{V}_{1-x}$	2.9–9.3	BI
12Re	BiPdSe	1.0	C2	$\text{CMo}_2\text{Zr}_{1-x}$	3.8–9.5	BI
	BiPdTe	1.2	C2	$\text{Co}_{1-0.9}\text{Nb}_{0.9-0.1}\text{Nb}$	8.5–17.9	
	BiPt	1.21	B8 ₁	$\text{Co}_{0.38}\text{Ni}_{1-0.62}\text{Ta}$	10.0–11.3	
	BiPtSe	1.45	C2	CNb (whiskers)	7.5–10.5	
	BiPtTe	1.15	C2	$\text{Co}_{0.984}\text{Nb}$	9.8	BI
	BiPtTe	0.155	Hexagonal	CNb (extrapolated)	~14	
12Re	Bi_2Pt	4.25	C15	$\text{Co}_{0.7-1.0}\text{Nb}_{0.3-0}$	6–11	BI
	Bi_2Rb	1.9–2.2		CNb_2	9.1	
	BiRc_2	2.06	B8 ₁	$\text{CNb}_2\text{Ta}_{1-x}$	8.2–13.9	
12Re	BiRh	3.2	Orthorhombic, like NiB_3	$\text{CNb}_2\text{Ti}_{1-x}$	<4.2–8.8	BI
al	Bi_3Rh		Hexagonal	$\text{CNb}_{0.8-0.9}\text{W}_{0.4-0.1}$	12.5–11.6	BI
				$\text{CNb}_{0.1-0.9}\text{Zr}_{0.9-0.1}$	4.2–8.4	BI
	Bi_4Rh	2.7		CRb_2 (gold)	0.023–0.151	Hexagonal
	Bi_3Sn	3.6–3.8		$\text{CRCo}_{0.01-0.08}\text{W}$	1.3–5.0	
	BiSn	3.8		$\text{CRCo}_{0.06}\text{W}$	5.0	
	Bi_3Sn_2	3.85–4.18		CTa	~11 (extrapolated)	
	Bi_3Sr	5.62	Li_2	$\text{Co}_{0.987}\text{Ta}$	9.7	
	Bi_3Te	0.75–1.0		$\text{Co}_{0.848-0.987}\text{Ta}$	2.04–9.7	
	Bi_3Ti_3	6.4	Cubic, disordered	CTa (film)	5.09	BI
	$\text{Bi}_{0.26}\text{Ti}_{0.74}$	4.4	Li_2 , ordered?	CTa_2	3.26	Li_3
				$\text{CTa}_{0.4}\text{Ti}_{0.6}$	4.8	BI
phases	$\text{Bi}_{0.16}\text{Ti}_{0.74}$	4.15		$\text{CTa}_{1-0.4}\text{W}_{0-0.6}$	8.5–10.5	BI
	Bi_2Y_3	2.25		$\text{CTa}_{0.2-0.9}\text{Zr}_{0.8-0.1}$	4.6–8.3	BI
	Bi_2Zn	0.8–0.9		CTe (excess C)	3.85	Cubic
	$\text{Bi}_{0.5}\text{Zr}_{0.7}$	1.51		$\text{CTi}_{0.5-0.7}\text{W}_{0.5-0.3}$	6.7–2.1	BI
	BiZr_3	2.4–2.8	Hexagonal	CW	1.0	
	CCs_2	0.020–0.135		CW_2	2.74	Li_3
	C_8K (gold)	0.55	Hexagonal, H-phase	CW_2	5.2	Cubic, f.c.
	CGaMo_2	3.7–4.1	BI	CaIr_2	6.15	C15
ase	$\text{CHf}_{0.3}\text{Mo}_{0.3}$	3.4	BI	$\text{Ca}_2\text{O}_3\text{Sr}_{1-x}\text{Ti}$	<0.1–0.55	
	$\text{CHf}_{0.3}\text{Mo}_{0.7}$	5.5	BI	($n = 3.7-11.0 \times 10^{19}$)		
	$\text{CHf}_{0.23}\text{Mo}_{0.75}$	6.6	BI	$\text{Ca}_{0.1}\text{O}_3\text{W}$	1.4–3.4	Hexagonal
	$\text{CHf}_{0.7}\text{Nb}_{0.3}$	6.1	BI	CaPb	7.0	
	$\text{CHf}_{0.4}\text{Nb}_{0.4}$	4.5	BI	CaRh_2	6.40	C15
	$\text{CHf}_{0.3}\text{Nb}_{0.3}$	4.8	BI	$\text{Cd}_{0.3-0.5}\text{Hg}_{0.7-0.5}$	1.70–1.92	
	$\text{CHf}_{0.4}\text{Nb}_{0.6}$	5.6	BI	CdHg	1.77, 2.15	Tetragonal
mbic	$\text{CHf}_{0.23}\text{Nb}_{0.75}$	7.0	BI	$\text{Cd}_{0.0075-0.05}\text{In}_{1-x}$	3.24–3.36	Tetragonal
	$\text{CHf}_{0.2}\text{Nb}_{0.8}$	7.8	BI	$\text{Cd}_{0.97}\text{Pb}_{0.03}$	4.2	
	$\text{CHf}_{0.9-0.1}\text{Ta}_{0.1-0.9}$	5.0–9.0	BI	CdSn	3.65	
al,	Ck (excess K)	0.55	Hexagonal	$\text{Cd}_{0.17}\text{Ti}_{0.83}$	2.3	
	C_8K	0.39	Hexagonal	$\text{Cd}_{0.18}\text{Ti}_{0.82}$	2.54	
	$\text{C}_{0.46-0.44}\text{Mo}_{0.60-0.56}$	9–13		CeCo_2	0.84	C15
	CMo	6.5, 9.26		$\text{CeCo}_{1.67}\text{Ni}_{0.33}$	0.46	C15
	CMo_2	12.2	Orthorhombic			

††See key at end of table.

Substance	T_c , °K	Crystal structure type††	Substance	T_c , °K	Crystal structure type††
CeCo _{1.67} Rh _{0.33}	0.47	Cl5	CuSe	1.5-2.0	Cl8
Ce ₂ Gd _{1-x} Ru ₂	3.2-5.2	Cl5	CuSe ₂	2.3-2.43	Cl8
CeIr ₃	3.34		CuSeTe	1.6-2.0	Cl8
CeIr ₅	1.82		Cu ₂ Sn _{1-x}	3.2-3.7	
Ce _{0.005} La _{0.995}	4.6		Cu ₂ Sn _{1-x} (film)		
Ce ₂ La _{1-x}	1.3-6.3		(made at 10°K)	3.6-7	
Ce ₂ Pr _{1-x} Ru ₂	1.4-5.3	Cl5	Cu ₂ Sn _{1-x} (film)		
Ce ₂ Pt _{1-x}	0.7-1.55		(made at 300°K)	2.8-3.7	
CeRu ₂	6.0	Cl5	CuTe ₂	<1.25-1.3	Cl8
Co ₂ Fe _{1-x} Si ₂	1.4 max.	Cl	CuTh ₂	3.49	Cl6
CoHf ₂	0.56	E9 ₃	Cu _{0.027} V	3.9-5.3	A2
CoLa ₃	4.28		Cu ₂ Zn _{1-x}	0.5-0.845	
CoLu ₃	~0.35		Er ₂ La _{1-x}	1.4-6.3	
Co _{0-0.01} Mo _{0.99} Re _{0.2}	2-10		Fe _{0.004} Mo _{0.996} Re _{0.2}	1-10	
Co _{0.02-0.10} Nb ₁ Rh _{0.98-0.90}	2.28-1.90	A15	Fe _{0.005} Ni _{0.05} Zr _{0.90}	~3.9	D10
Co ₂ Ni _{1-x} Si ₂	1.4 max.	Cl	Fe ₂ Th ₇	1.86	Fe in α -Ti
Co _{0.3} Rh _{0.5} Si ₂	2.5		Fe ₂ Ti _{1-x}	3.2 max.	Fe in β -Ti
Co ₂ Rh _{1-x} Si ₂	3.65 max.		Fe ₂ Ti _{1-x}	3.7 max.	
Co- _{0.3} Sc- _{0.7}	~0.35		Fe ₂ Ti _{0.6} V _{1-x}	6.8 max.	
CoSi ₃	1.40, 1.22	Cl	FeU ₆	3.86	D2 ₂
Co ₂ Th ₇	1.83	D10 ₂	Fe _{0.1} Zr _{0.9}	1.0	A3
Co ₂ Ti _{1-x}	2.8 max.	Co in α -Ti	Ga _{0.5} Gc _{0.5} Nb ₃	7.3	A15
Co ₂ Ti _{1-x}	3.8 max.	Co in β -Ti	GaLa ₃	5.84	
CoTi ₂	3.44	E9 ₃	Ga ₂ Mo	9.5	
CoTi	0.71	A2	GaMo ₃	0.76	A15
CoU	1.7	B2, distorted	Ga ₂ Mo	9.8	
CoU ₆	2.29	D2 ₂	GaN (black)	5.85	B4
Co _{0.28} Y _{0.72}	0.34		GaNb ₃	14.5	A15
CoY ₃	<0.34		Ga ₂ Nb ₃ Sn _{1-x}	14-18.37	A15
CoZr ₂	6.3	Cl6	Ga ₂ Pt _{0.3}	2.9	Cl
Co _{0.1} Zr _{0.9}	3.9	A3	GaPt	1.74	B20
Cr _{0.6} Ir _{0.4}	0.4	Hexagonal, c.p.	GaSb (120 kbar, 77°K, annealed)	4.24	A5
Cr _{0.65} Ir _{0.35}	0.59	Hexagonal, c.p.	GaSb (unannealed)	~5.9	
Cr _{0.7} Ir _{0.3}	0.76	Hexagonal, c.p.	Ga _{0.1} Sn _{1-x} (quenched)	3.47-4.18	
Cr _{0.72} Ir _{0.28}	0.83		Ga _{0.1} Sn _{1-x} (annealed)	2.6-3.85	
Cr ₃ Ir	0.45	A15	Ga ₃ V ₂	3.55	Tetragonal, Mn ₂ Hg ₈ type
Cr _{0-0.1} Nb _{1-0.9}	4.6-9.2	A2			
Cr _{0.80} Os _{0.20}	2.5	Cubic			
Cr ₂ Re _{1-x}	1.2-5.2				
Cr _{0.40} Re _{0.60}	2.15	D8 ₈			
Cr _{0.8-0.6} Rh _{0.2-0.4}	0.5-1.10	A3			
Cr ₃ Ru (annealed)	3.3	A15			
Cr ₂ Ru	2.02	D8 ₈			
Cr _{0.1-0.3} Ru _{0.9-0.3}	0.34-1.65	A3			
Cr ₂ Ti _{1-x}	3.6 max.	Cr in α -Ti			
Cr ₂ Ti _{1-x}	4.2 max.	Cr in β -Ti			
Cr ₂ Ti _{1-x}	5.6				
Cr _{0.1} Ti _{0.9} Vo _{0.6}	0.75	β -phase			
Cr _{0.0175} U _{0.9825}	1.12	Hexagonal			
Cr _{0.32} O ₃ W	3.75				
Cu _{0.15} In _{0.85} (film)	4.4				
Cu _{0.04-0.08} In _{1-x}	5.85				
CuLa	5.7-7.7				
Cu ₂ Pb _{1-x}	1.62	B18			
CuS	1.48-1.53	Cl8			
CuS ₂					
			CuSe	1.5-2.0	Cl8
			CuSe ₂	2.3-2.43	Cl8
			CuSeTe	1.6-2.0	Cl8
			Cu ₂ Sn _{1-x}	3.2-3.7	
			Cu ₂ Sn _{1-x} (film)		
			(made at 10°K)	3.6-7	
			Cu ₂ Sn _{1-x} (film)		
			(made at 300°K)	2.8-3.7	
			CuTe ₂	<1.25-1.3	Cl8
			CuTh ₂	3.49	Cl6
			Cu _{0.027} V	3.9-5.3	A2
			Cu ₂ Zn _{1-x}	0.5-0.845	
			Er ₂ La _{1-x}	1.4-6.3	
			Fe _{0.004} Mo _{0.996} Re _{0.2}	1-10	
			Fe _{0.005} Ni _{0.05} Zr _{0.90}	~3.9	D10
			Fe ₂ Th ₇	1.86	Fe in α -Ti
			Fe ₂ Ti _{1-x}	3.2 max.	Fe in β -Ti
			Fe ₂ Ti _{1-x}	3.7 max.	
			Fe ₂ Ti _{0.6} V _{1-x}	6.8 max.	
			FeU ₆	3.86	D2 ₂
			Fe _{0.1} Zr _{0.9}	1.0	A3
			Ga _{0.5} Gc _{0.5} Nb ₃	7.3	A15
			GaLa ₃	5.84	
			Ga ₂ Mo	9.5	
			GaMo ₃	0.76	A15
			Ga ₂ Mo	9.8	
			GaN (black)	5.85	B4
			GaNb ₃	14.5	A15
			Ga ₂ Nb ₃ Sn _{1-x}	14-18.37	A15
			Ga ₂ Pt _{0.3}	2.9	Cl
			GaPt	1.74	B20
			GaSb (120 kbar, 77°K, annealed)	4.24	A5
			GaSb (unannealed)	~5.9	
			Ga _{0.1} Sn _{1-x} (quenched)	3.47-4.18	
			Ga _{0.1} Sn _{1-x} (annealed)	2.6-3.85	
			Ga ₃ V ₂	3.55	Tetragonal, Mn ₂ Hg ₈ type
			GaV ₃	16.8	A15
			GaV _{2.1-3.5}	6.3-14.45	A15
			GaV _{4.5}	9.15	
			Ga ₂ Zr	1.38	
			Gd ₂ La _{1-x}	<1.0-5.5	
			Gd ₂ O ₇ Y _{1-x}	1.4-4.7	
			Gd ₂ Ru ₂ Th _{1-x}	3.6 max.	Cl5
			Gelr	4.7	B31
			Ge ₂ La	1.49, 2.2	Orthorhombic, distorted ThSi ₂ -type
			GeMo ₃	1.43	A15
			GeNb ₂	1.9	
			GeNb ₃ (quenched)	6-17	A15
			Ge _{0.25} Nb _{0.75}	6	A15
			Ge ₂ Nb ₃ Sn _{1-x}	17.6-18.0	A15
			Ge _{0.5} Nb _{0.5} Sn _{0.5}	11.3	

††See key at end of table.

SELECTED SUPERCONDUCTIVE COMPOUNDS AND ALLOYS (Continued)

Substance	T_c , °K	Crystal structure type††	Substance	T_c , °K	Crystal structure type††
GePt	0.40	B3I	InSb	2.1	
Ge ₃ Rh ₃	2.12	Orthorhombic, related to InNi ₂	(InSb) _{0.95-0.10} Sn _{0.05-0.90} (various heat treatments)	3.8-5.1	
			(InSb) _{0-0.07} Sn _{1-0.93}	3.67-3.74	
Ge ₂ Sc	1.3		In ₃ Sn	~5.5	
Ge ₃ Te ₄			In ₂ Sn _{1-x}	3.4-7.3	
($n = 1.06 \times 10^{23}$)			In _{0.82-1} Te		
Ge ₂ Te _{1-x}	1.55-1.80	Rhombohedral	($n = 0.83-1.71 \times 10^{23}$)	1.02-3.45	BI
($n = 8.5-64 \times 10^{23}$)			In _{1.000} Te _{1.002}	3.5-3.7	BI
GeV ₅	6.01	BI	In ₃ Te ₄		
Ge ₂ Y	3.80	C ₆	($n = 0.47 \times 10^{23}$)	1.15-1.25	Rhombohedral
Ge _{1.62} Y	2.4		In ₂ Tl _{1-x}	2.7-3.374	
Hg _{0.31} Nb _{0.67}	7.28	Cubic, b.c.	In _{0.8} Tl _{0.2}	3.223	
Hg _{0.1} Nb _{0.9}	7.38	Cubic, b.c.	In _{0.62} Tl _{0.38}	2.760	
Hg _{0.05} Nb _{0.95}	7.83	Cubic, b.c.	In _{0.78-0.69} Tl _{0.22-0.31}	3.18-3.32	Tetragonal
Hg _{0.12} Ta _{0.88}	2.81	Cubic, b.c.	In _{0.69-0.62} Tl _{0.31-0.38}	2.98-3.3	Cubic, f.c.
Hg _{0.08} Ta _{0.92}	3.26	Cubic, b.c.	Ir ₂ La	0.48	C15
Hg _{0.04} Ta _{0.96}	3.62	Cubic, b.c.	Ir ₃ La	2.32	D10 ₂
HfNi _{0.989}	6.6	BI	Ir ₃ La ₇	2.24	D10 ₂
Hf _{0-0.5} Nb _{1-0.5}	8.3-9.5	A2	Ir ₃ La	2.13	
Hf _{0.75} Nb _{0.25}	> 4.2		Ir ₃ Lu	2.47	C15
HfO ₈₂	2.69	C14	Ir ₃ Lu	2.89	C15
HfRe ₂	4.80	C14	IrMo	< 1.0	A3
Hf _{0.14} Re _{0.86}	5.86	A12	IrMo ₂	8.8	A15
Hf _{0.99-0.96} Rh _{0.01-0.04}	0.85-1.51		IrMo ₃	6.8	D8 ₈
Hf _{0-0.55} Ta _{1-0.45}	4.4-6.5	A2	IrNb ₃	1.9	A15
HfV ₃	8.9-9.6	C15	Ir _{0.2} Nb _{0.6}	9.8	D8 ₈
Hg ₂ In _{1-x}	3.14-4.55		Ir _{0.35} Nb _{0.65}	2.32	D8 ₈
HgIn	3.81		IrNb	7.9	D8 ₈
Hg ₂ K	1.20	Orthorhombic	Ir _{0.02} Nb ₃ Rh _{0.98}	2.43	A15
Hg ₃ K	3.18		Ir _{0.05} Nb ₃ Rh _{0.95}	2.38	A15
Hg ₄ K	3.27		Ir _{0.38} O _{0.14} Tl _{0.573}	5.5	E9 ₃
Hg ₈ K	3.42		Ir _{0.265} O _{0.035} Tl _{0.65}	2.30	E9 ₃
Hg ₃ Li	1.7	Hexagonal	Ir ₂ Os _{1-x}	0.3-0.98 (max.)-0.6	
Hg ₂ Na	1.62	Hexagonal	IrOsY	2.6	C15
Hg ₄ Na	3.05		Ir _{1.5} Os _{0.5}	2.4	C14
Hg ₂ Pb _{1-x}	4.14-7.26		Ir ₃ Sc	2.07	C15
HgSn	4.2		Ir _{2.5} Sc	2.46	C15
Hg ₂ Tl _{1-x}	2.30-4.109		IrSn ₂	0.65-0.78	C1
Hg ₃ Tl ₂	3.86		Ir ₂ Sr	5.70	C15
Ho ₂ La _{1-x}	1.3-6.3		Ir _{0.5} Te _{0.5}	~ 3	
InLa ₃	9.83, 10.4		IrTe ₃	1.18	C2
InLa ₃ (0-35, kbar)	9.75-10.55	Li ₂	IrTh	< 0.37	B _f
In _{1-0.86} Mg _{0-0.14}	3.395-3.363		Ir ₃ Th	6.50	C15
InNb ₃			Ir ₃ Th	4.71	
(high pressure and temp.)	4-8, 9.2	A15	Ir ₃ Th ₇	1.52	D10 ₂
In _{0-0.3} Nb ₃ Sn _{1-0.7}	18.0-18.19	A15	Ir ₃ Th	3.93	D2 ₂
In _{0.5} Nb ₃ Zr _{0.5}	6.4		IrTi ₃	5.40	A15
In _{0.11} O ₃ W	< 1.25-2.8	Hexagonal	IrV ₃	1.39	A15
In _{0.95-0.85} Pb _{0.05-0.15}	3.6-5.05		IrW ₃	3.82	
In _{0.98-0.91} Pb _{0.02-0.09}	3.45-4.2		Ir _{0.28} W _{0.72}	4.49	
InPb	6.65		Ir ₂ Y	2.18, 1.38	C15
InPd	0.7	B2	Ir _{0.69} Y _{0.31}	1.98, 1.44	C15
InSb (quenched from 170 kbar into liquid N ₂)	4.8	Like A5	Ir _{0.70} Y _{0.30}	2.16	C15

††See key at end of table.

SELECTED SUPERCONDUCTIVE COMPOUNDS AND ALLOYS (Continued)

Substance	T_c , °K	Crystal structure type††	Substance	T_c , °K	Crystal structure type††
Ir ₂ Y	1.09	C15	Mo ₃ Si	1.30	A15
Ir ₂ Y ₃	1.61		MoSi _{0.7}	1.34	
Ir ₂ Y _{1-x}	0.3-3.7		Mo ₃ SiV _{1-x}	4.54-16.0	A15
Ir ₂ Zr	4.10	C15	Mo ₂ Tc _{1-x}	10.8-15.8	
Ir _{0.1} Zr _{0.9}	5.5	A3	Mo _{0.16} Ti _{0.84}	4.18, 4.25	
K _{0.27-0.31} O ₃ W	0.50	Hexagonal	Mo _{0.913} Ti _{0.087}	2.95	
K _{0.40-0.51} O ₃ W	1.5	Tetragonal	Mo _{0.04} Ti _{0.96}	2.0	Cubic
La _{0.33} Lu _{0.67}	2.2	Hexagonal, La type	Mo _{0.025} Ti _{0.975}	1.8	
La _{0.8} Lu _{0.2}	3.4	Hexagonal, La Type	Mo ₂ U _{1-x}	0.7-2.1	
LaMg ₂	1.05	C15	Mo ₂ V _{1-x}	0-5.3	
LaN	1.35		Mo ₂ Zr	4.27-4.75	C15
LaOs ₂	6.5	C15	NNb (whiskers)	10-14.5	
LaPt ₂	0.46	C15	NNb (diffusion wires)	16.10	
La _{0.28} Pt _{0.72}	0.54	C15	NNb (film)	6-9	BI
LaRh ₃	2.60		N _{0.988} Nb	14.9	BI
LaRh ₂	1.62		N _{0.824-0.988} Nb	14.4-15.3	Cubic and tetragonal
La ₂ Rh ₃	2.58	D10 ₃	N _{0.70-0.795} Nb	11.3-12.9	
La ₂ Ru ₃	1.63	C15	NNb ₂ O ₇	13.5-17.0	BI
La ₂ Se ₄	8.6	D7 ₃	NNb ₂ O ₇	6.0-11	
LaSi ₂	2.3	D7 ₃	N _{100-42 wt%Nb} -58 wt%Ti	15-16.8	
La ₂ Y _{1-x}	1.7-5.4	C _c	N _{100-75 wt%Nb} -25 wt%Zr	12.5-16.35	
LaZn	1.04	B2	NNb ₂ Zr _{1-x}	9.8-13.8	BI
LiPb	7.2		N _{0.85} Nb _{0.85} Zr _{0.15}	13.8	BI
LuOs ₂	3.49	C14	N ₂ O ₂ Ti ₄	2.9-5.6	Cubic
Lu _{0.275} Rh _{0.725}	1.27	C15	N ₂ O ₂ V ₄	5.8-8.2	Cubic
LuRh ₃	0.49		N _{0.34} Re	4-5	Cubic, f.c.
LuRu ₂	0.86	C14	NTa	12-14	BI
Mg _{0.47} Tl _{0.53}	2.75	B2	NTa (film)	(extrapolated)	
Mg ₂ Nb	5.6		N _{0.6-0.987} Ti	4.84	BI
Mn ₂ Ti _{1-x}	2.3 max.	Mn in α-Ti	N _{0.82-0.99} V	<1.17-5.8	BI
Mn ₂ Ti _{1-x}	1.1-3.0	Mn in β-Ti	NZr	2.9-7.9	BI
MnU ₆	2.32	D2 ₈	N _{0.906-0.984} Zr	9.8	BI
MoN	12	Hexagonal	N _{0.906-0.984} Zr	3.0-9.5	BI
Mo ₂ N	5.0	Cubic, f.c.	N _{0.28-0.35} O ₃ W	0.56	Tetragonal
Mo ₂ Nb _{1-x}	0.016-9.2		N _{0.28} Pb _{0.72}	7.2	
Mo ₂ Os	7.2	A15	NbO	1.25	A12
Mo _{0.62} Os _{0.38}	5.65	D8 ₈	NbO ₂	2.52	A15
Mo ₃ P	5.31	DO ₄	Nb ₃ Os	1.05	D8 ₈
Mo _{0.5} Pd _{0.5}	3.52	A3	Nb _{0.6} Os _{0.4}	1.89, 1.78	A15
Mo ₃ Re	10.0		Nb ₃ Os _{0.02-0.10} Rh _{0.98-0.90}	2.42-2.30	A15
Mo ₂ Re _{1-x}	1.2-12.2		Nb _{0.6} Pd _{0.4}	1.60	D8 ₈ plus cubic
MoRe ₃	9.25, 9.89	A12	Nb ₃ Pd _{0.02-0.10} Rh _{0.98-0.90}	2.49-2.55	A15
Mo _{0.42} Re _{0.58}	6.35	D8 ₈	Nb _{0.62} Pt _{0.38}	4.21	D8 ₈
Mo _{0.52} Re _{0.48}	11.1		Nb ₃ Pt	10.9	A15
Mo _{0.57} Re _{0.43}	14.0		Nb ₂ Pt ₃	3.73	D8 ₈
Mo _{0.60} Re _{0.40}	10.6		Nb ₃ Pt _{0.02-0.98} Rh _{0.98-0.02}	2.52-9.6	A15
MoRh	1.97	A3	Nb _{0.38-0.18} Re _{0.62-0.82}	2.43-9.70	A15
Mo ₂ Rh _{1-x}	1.5-8.2	Cubic, b.c.	Nb ₃ Rh	2.64	A15
MoRu	9.5-10.5	A3	Nb _{0.40} Rh _{0.60}	4.21	D8 ₈ plus other
Mo _{0.61} Ru _{0.39}	7.18	D8 ₈	Nb ₃ Rh _{0.98-0.90} Ru _{0.02-0.10}	2.42-2.44	A15
Mo _{0.2} Ru _{0.8}	1.66	A3	Nb ₂ Ru _{1-x}	1.2-4.8	
Mo ₃ Sb ₄	2.1		NbS ₂	6.1-6.3	Hexagonal, NbSe ₂ type

†w/o denotes weight percent.

††See key at end of table.

SELECTED SUPERCONDUCTIVE COMPOUNDS AND ALLOYS (Continued)

Substance	$T_c, ^\circ K$	Crystal structure type††	Substance	$T_c, ^\circ K$	Crystal structure type††
NbS ₂	5.0-5.5	Hexagonal, three-layer type	Os ₂ Zr	3.0	C14
Nb ₃ Sb _{0.9-0.7} Sn _{1-0.3}	6.8-18	Al5	Os ₂ Zr _{1-x}	1.50-5.6	
NbSe ₂	5.15-5.62	Hexagonal, NbS ₂ type	PPb	7.8	
Nb _{1-1.05} Se ₂	2.2-7.0	Hexagonal, NbS ₂ type	PPd _{3.0-3.2}	<0.35-0.7	DO ₁₁
Nb ₃ Si	1.5	Li ₂	F ₃ Pd ₃ (high temperature)	1.0	Rhombohedral
Nb ₃ SiSnV ₃	4.0		F ₃ Pd ₃ (low temp.)	0.70	Complex
Nb ₃ Sn	18.05	Al5	PRh ₂	1.22	Cl
Nb _{0.8} Sn _{0.2}	18.18, 18.5	Al5	PW ₃	1.3	DO ₂
Nb ₃ Sn _{1-x} (film)	2.6-18.5		Pb ₂ Pd	2.95	C16
NbSn ₂	2.60	Orthorhombic	Pb ₂ Pt	2.80	Related to C16
Nb ₃ Sn ₂	16.6	Tetragonal	Pb ₂ Rh	2.66	C16
NbSnTa ₂	10.8	Al5	PbTe (plus 0.1 w/o Pb)†	5.19	
Nb ₃ SnTa	16.4	Al5	PbTe (plus 0.1 w/o Tl)†	5.24-5.27	
Nb _{2.3} SnTa _{0.5}	17.6	Al5	PbTl _{0.27}	6.43	
Nb _{2.75} SnTa _{0.25}	17.8	Al5	PbTl _{0.17}	6.73	
Nb _{0.9} SnTa _{2(1-x)}	6.0-18.0		PbTl _{0.12}	6.88	
NbSnTaV	6.2	Al5	PbTl _{0.075}	6.98	
Nb ₃ SnTa _{0.5} V _{0.5}	12.2	Al5	PbTl _{0.04}	7.06	
NbSnV ₂	5.5	Al5	Pb _{1-0.26} Tl _{0-0.74}	7.20-3.68	
Nb ₃ SnV	9.8	Al5	PbTl ₂	3.75-4.1	
Nb _{2.3} SnV _{0.5}	14.2	Al5	Pb ₂ Zr ₅	4.60	D8 ₈
Nb ₃ Ta _{1-x}	4.4-9.2	A2	PbZr ₃	0.76	Al5
NbTc ₃	10.5	Al2	Pd _{0.9} Pt _{0.1} Tc ₂	1.65	C6
Nb ₃ Ti _{1-x}	0.6-9.8		Pd _{0.05} Ru _{0.05} Zr _{0.9}	~9	
Nb _{0.8} Ti _{0.4}	9.8		Pd ₃ S (quenched)	1.63	Cubic
Nb ₃ U _{1-x}	1.95 max.		PdSb ₂	1.25	C2
Nb _{0.88} V _{0.12}	5.7	A2	PdSb	1.50	B8 ₁
Nb _{0.75} Zr _{0.25}	10.8		PdSbSe	1.0	C2
Nb _{0.66} Zr _{0.33}	10.8		PdSbTe	1.2	C2
Ni _{0.5} Tb _{0.5}	1.98	D10 ₂	Pd ₃ Se	0.42	Tetragonal
NiZn ₂	1.52		Pd _{1-x} Se	0.66	Like Pd ₄ Te
Ni _{0.17} Zr _{0.9}	1.5	A3	Pd _{3.5} Se	2.3	
O ₃ Rb _{0.27-0.29} W	1.98	Hexagonal	Pd ₂ Se _{1-x}	2.5 max.	
O ₃ SrTi			PdSi	0.93	B31
(n = 1.7-12.0 × 10 ¹⁹)	0.12-0.37		PdSn	0.41	B31
O ₃ SrTi			PdSn ₂	3.34	
(n = 10 ¹⁸ -10 ²¹)	0.05-0.47		Pd ₃ Sn	0.41	C37
O ₃ SrTi			Pd ₃ Sn ₂	0.47-0.64	B8 ₂
(n = ~10 ²⁰)	0.47		PdTe	2.3, 3.85	B8 ₁
OTi	0.58		PdTe _{1.02-1.08}	2.56-1.88	B8 ₁
O ₃ St _{0.08} W	2-4	Hexagonal	PdTe ₂	1.69	C6
O ₃ Tl _{0.10} W	2.0-2.14	Hexagonal	PdTe _{2.1}	1.89	C6
OV ₃ Zr ₃	7.5	E9 ₃	PdTe _{2.3}	1.85	C6
OW ₃ (film)	3.35, 1.1	Al5	Pd _{1.1} Te	4.07	B8 ₂
OsReY	2.0	C14	PdTh ₂	0.85	C16
Os ₂ Sc	4.6	C14	Pd _{0.1} Ta _{0.9}	7.5	A3
OsTa	1.95	Al2	PtSb	2.1	B8 ₁
Os ₃ Th ₇	1.51	D10 ₂	PtSi	0.88	B31
Os ₂ W _{1-x}	0.9-4.1		PtSn	0.37	B8 ₁
OsW ₃	~3		PtTe	0.59	Orthorhombic
Os ₂ Y	4.7	C14	PtTh	0.44	B _f
			Pt ₃ Th ₇	0.98	D10 ₂
			Pt ₄ Th	3.13	

†w/o denotes weight percent.

††See key at end of table.

SELECTED SUPERCONDUCTIVE COMPOUNDS AND ALLOYS (Continued)

Substance	T_c , °K	Crystal structure type††	Substance	T_c , °K	Crystal structure type††
PtTi ₃	0.58	A15	Ru ₃ Y	1.52	C14
Pt _{0.92} O _{0.98}	0.87	β-phase	Ru ₂ Zr	1.84	C14
PtV _{2.5}	1.36	A15	Ru _{0.1} Zr _{0.9}	5.7	A3
PtV ₃	2.87–3.20	A15	SbSn	1.30–1.42, 1.42–2.37	B1 or distorted B1
PtV _{3.3}	1.26	A15	SbTi ₃	5.8	A15
Pt _{0.5} W _{0.5}	1.45	A1	Sb ₂ Tl ₃	5.2	
Pt ₁ W _{1-x}	0.4–2.7		Sb _{0.01-0.03} V _{0.99-0.97}	3.76–2.63	A2
Pt ₂ Y	0.90		SbV ₃	0.80	A15
Pt ₃ Y	1.57, 1.70	C15	Si ₂ Th	3.2	C ₂ , α-phase
Pt ₃ Y ₇	0.82	D10 ₂	Si ₂ Th	2.4	C32, β-phase
PtZr	3.0	A3	SiV ₃	17.1	A15
Rc _{0.64} Ta _{0.36}	1.46	A12	Si ₃ V ₃ Al _{0.1}	14.05	A15
Rc ₂₄ Ti ₁₅	6.60	A12	Si _{0.9} V ₃ B _{0.1}	15.8	A15
Rc ₂ Ti _{1-x}	6.6 max.		Si _{0.9} V ₃ C _{0.1}	16.4	A15
Rc _{0.76} V _{0.24}	4.52	D8 ₈	SiV ₂ ,C _{0.3}	11.3	A15
Rc _{0.92} V _{0.08}	6.8	A3	Si _{0.9} V ₃ G _{0.1}	14.0	A15
Rc _{0.6} W _{0.4}	6.0		SiV ₂ ,M _{0.3}	11.7	A15
Rc _{0.5} W _{0.5}	5.12	D8 ₈	SiV ₂ ,Nb _{0.3}	12.8	A15
Rc ₂ Y	1.83	C14	SiV ₂ ,Ru _{0.3}	2.9	A15
Rc ₂ Zr	5.9	C14	SiV ₂ ,Ti _{0.3}	10.9	A15
Rc ₂ Zr	7.40	A12	SiV ₂ ,Zr _{0.3}	13.2	A15
Rh ₁ S ₁₅	5.8	Cubic	Si ₂ W ₃	2.8, 2.84	
Rh _{-0.24} Sc _{-0.76}	0.88, 0.92		Sn _{0.174-0.104} Ta _{0.826-0.896}	6.5–<4.2	A15
Rh ₃ Se _{1-x}	6.0 max.		SnTa ₃	8.35	A15, highly ordered
Rh ₃ Sr	6.2	C15	SnTa ₃	6.2	A15, partially ordered
Rh _{0.4} Ta _{0.6}	2.35	D8 ₈	SnTaV ₂	2.8	A15
RhTe ₂	1.51	C2	SnTa ₂ V	3.7	A15
Rh _{0.67} Te _{0.33}	0.49		Sn ₂ Te _{1-x}		
Rh ₃ Te _{1-x}	1.51 max.		(n = 10.5–20 × 10 ¹⁹)	0.07–0.22	B1
RhTh	0.36	B ₇	Sn ₂ Tl _{1-x}	2.37–5.2	B1
Rh ₂ Th ₇	2.15	D10 ₂	SnV ₃	3.8	B2
Rh ₂ Th	1.07		Sn _{0.02-0.057} V _{0.98-0.943}	2.87–~1.6	B2
Rh ₂ Ti _{1-x}	2.25–3.95		Ta _{0.025} Ti _{0.975}	1.3	B1
Rh _{0.02} U _{0.98}	0.96		Ta _{0.05} Ti _{0.95}	2.9	B1
RhV ₃	0.38	A15	Ta _{0.05-0.75} V _{0.95-0.25}	4.30–2.65	B1
RhW	~3.4	A3	Ta _{0.8-1} W _{0.2-0}	1.2–4.4	B1
RhY ₃	0.65		Tc _{0.1-0.4} W _{0.9-0.6}	1.25–7.18	B2
Rh ₂ Y ₃	1.48		Tc _{0.50} W _{0.50}	7.52	B2
Rh ₂ Y	1.07	C15	Tc _{0.45} W _{0.40}	7.88	B2
Rh ₂ Y	0.56		Tc ₂ Zr	9.7	B3
RhZr ₂	10.8	C16	Th _{0-0.55} Y _{1-0.45}	1.2–1.8	B3
Rh _{0.005} Zr (annealed)	5.8		Ti _{0.70} V _{0.30}	6.14	Cubic
Rh _{0-0.45} Zr _{1-0.55}	2.1–10.8	Hexagonal, c.p.	Ti ₁ V _{1-x}	0.2–7.5	
Rh ₂ Zr _{0.9}	9.0		Ti _{0.5} Zr _{0.5} (annealed)	1.23	
Ru ₃ Sc	1.67	C14	Ti _{0.5} Zr _{0.5} (quenched)	2.0	
Ru ₃ Th	3.56	C15	V ₂ Zr	8.80	C15
RuTi	1.07	B2	V _{0.16} Zr _{0.74}	~5.9	C2
Ru _{0.05} Ti _{0.95}	2.5		W ₂ Zr	2.16	C15
Ru _{0.1} Ti _{0.9}	3.5				
Ru _{0.110.6} V _{0.5}	6.6 max.				
Ru _{0.45} V _{0.55}	4.0	B2			
RuW	7.5	A3			

†† See key at end of table.

* See "H₂

CRITICAL FIELD DATA

Substance	H_{c1} oersteds	Substance	H_{c2} oersteds
Ag_2F	2.5	InSb	1,100
$\text{Ag}_2\text{NO}_{11}$	57	$\text{In}_2\text{Ti}_{1-x}$	252-284
Al_2CMO_3	1,700	$\text{In}_{0.8}\text{Ti}_{0.2}$	252
BaBi_3	740	$\text{Mg}_{0.47}\text{Ti}_{0.53}$	220
Bi_2Pt	10	$\text{Mo}_{0.16}\text{Ti}_{0.84}$	<985
Bi_2Sr	530	NbSn_2	620
Bi_2Ti_3	>400	$\text{PbTi}_{0.27}$	756
CoSn	>266	$\text{PbTi}_{0.17}$	796
CoSi_2	105	$\text{PbTi}_{0.12}$	849
$\text{Co}_{0.1}\text{Ti}_{0.9}\text{V}_{0.6}$	1,360	$\text{PbTi}_{0.075}$	880
$\text{In}_{1-0.86}\text{Mg}_{0-0.14}$	272.4-259.2	$\text{PbTi}_{0.04}$	864

KEY TO CRYSTAL STRUCTURE TYPES

"Strukturbericht" type*	Example	Class	"Strukturbericht" type*	Example	Class
A1	Cu	Cubic, f.c.	C15	AuBe_2	Cubic
A2	W	Cubic, b.c.	C16	CuAl_2	Tetragonal, b.c.
A3	Mg	Hexagonal, close packed	C18	FeS_2	Orthorhombic
A4	Diamond	Cubic, f.c.	C22	Fe_2P	Trigonal
A5	White Sn	Tetragonal, b.c.	C23	PbCl_2	Orthorhombic
A6	In	Tetragonal, b.c. (f.c. cell usually used)	C32	AlB_3	Hexagonal
A7	As	Rhombohedral	C36	MgNi_2	Hexagonal
A8	Se	Trigonal	C37	Co_2Si	Orthorhombic
A10	Hg	Rhombohedral	C49	ZrSi_3	Orthorhombic
A12	α -Mn	Cubic, b.c.	C54	TiSi_2	Orthorhombic
A13	β -Mn	Cubic	C	Si_2Th	Tetragonal, b.c.
A15	" β -W" (WO_3)	Cubic	DO ₃	BiF_3	Cubic, f.c.
B1	NaCl	Cubic, f.c.	DO ₁₁	Fe_2C	Orthorhombic
B2	CsCl	Cubic	DO ₁₈	Na_2As	Hexagonal
B3	ZnS	Cubic	DO ₁₉	Ni_2Sn	Hexagonal
B4	ZnS	Hexagonal	DO ₂₀	NiAl_3	Orthorhombic
B8 ₁	NiAs	Hexagonal	DO ₂₂	TiAl_3	Tetragonal
B8 ₂	Ni_2In	Hexagonal	DO ₂₄	Ni_2P	Tetragonal, b.c.
B10	PbO	Tetragonal	D1 ₁	Al_2B_6	Tetragonal, b.c.
B11	γ -CuTi	Tetragonal	D1 ₂	PtSn_4	Orthorhombic
B17	PTs	Tetragonal	D2 ₁	CaB_6	Cubic
B18	CuS	Hexagonal	D2 ₂	MnU_6	Tetragonal, b.c.
B20	FeSi	Cubic	D2 ₄	CaZn_5	Hexagonal
B27	FeB	Orthorhombic	D5 ₂	La_2O_3	Trigonal
B31	MnP	Orthorhombic	D5 ₄	Sb_2S_3	Orthorhombic
B32	NaTi	Cubic, f.c.	D7 ₃	Th_2P_4	Cubic, b.c.
B34	PdS	Tetragonal	D7 ₄	Ta_2B_4	Orthorhombic
B ₇	δ -CrB	Orthorhombic	D8 ₁	$\text{Fe}_2\text{Zn}_{10}$	Cubic, b.c.
B ₈	MoB	Tetragonal, b.c.	D8 ₂	Cu_2Zn_8	Cubic, b.c.
B ₉	WC	Hexagonal	D8 ₃	Cu_2Al_4	Cubic
B ₁₀	γ -MoC	Hexagonal	D8 ₄	Mn_2Si_3	Hexagonal
C1	CaF_2	Cubic, f.c.	D8 ₅	CrFe	Tetragonal
C1 ₈	MgAgAs	Cubic, f.c.	D8 ₆	Mo_2B_3	Rhombohedral
C2	FeS_2	Cubic	D10 ₁	Fe_2Th	Hexagonal
C6	CdI_2	Trigonal	E2 ₁	CaTiO_3	Cubic
C11b	MoSi_2	Tetragonal, b.c.	E9 ₃	$\text{Fe}_2\text{W}_2\text{C}$	Cubic, f.c.
C12	CaSi_2	Rhombohedral	L1 ₀	CuAu	Tetragonal
C14	MgZn_2	Hexagonal	L1 ₂	Cu_3Au	Cubic
C15	Cu_2Mg	Cubic, f.c.	L2 ₈	ThH_2	Tetragonal, b.c.
			L3	Fe_2N	Hexagonal

*See "Handbook of Lattice Spacing and Structures of Metals", W.B. Pearson, Vol. I, Pergamon Press, 1958, p. 79, and Vol. II, Pergamon Press, 1967, p. 3.

HIGH CRITICAL MAGNETIC-FIELD SUPERCONDUCTIVE COMPOUNDS AND ALLOYS

With Critical Temperatures, H_{c1} , H_{c2} , H_{c3} , and the Temperature of Field Observations, T_{obs}

Substance	T_c , °K	H_{c1} , kg	H_{c2} , kg	H_{c3} , kg	T_{obs} , °K†
Al_2CMo_3	9.8-10.2	0.091	156		1.2
$AlNb_3$		0.375			
$Ba_2O_3Sr_{1-x}Ti$	<0.1-0.55	0.0039 max.			
$Bi_{0.5}Cd_{0.5}Pb_{0.25}Sn_{0.15}$			>24		3.06
Bi_2Pb_{1-x}	7.35-8.4	0.122 max.	~30 max.		4.2
$Bi_{0.58}Pb_{0.42}$	8.8		15		4.2
$Bi_{1.5}W_0.5Pb_{0.25}Sn_{0.15}$			2.32		
$Bi_{0.095}Pb_{0.905}$		0.29	2.8		
$Bi_{0.02}Pb_{0.98}$		0.46	0.73		
$Bi_{0.3}Pb_{0.3}Sn_{0.16}$			>25		3.06
$Bi_{1-0.85}Sn_{0.85}$			0-0.032		3.7
Bi_2Ti_3	6.4		>5.56		3.35
C_6K (excess K)	0.55		0.160 (H.c)		0.32
			0.730 (H.c)		0.32
			0.025 (H.c)		0.32
			0.250 (H.c)		0.32
$C_{0.44}Mo_{0.56}$	12.5-13.5	0.087	98.5		1.2
CNb	8-10	0.12	16.9		4.2
$CNb_{0.4}Ta_{0.6}$	10-13.6	0.19	14.1		1.2
CTa	9-11.4	0.22	4.6		1.2
$Cd_2O_3Sr_{1-x}Ti$	<0.1-0.55	0.002-0.004			
$Cd_{0.1}Hg_{0.9}$ (by weight)		0.23	0.34		2.04
$Cd_{0.05}Hg_{0.95}$		0.28	0.31		2.16
$Cd_{0.10}Ti_{0.30}V_{0.60}$	5.6	0.071	84.4		0
GaN	5.85	0.725			4.2
Ga_2Nb_{1-x}			>28		4.2
GaSb (annealed)	4.24		2.64		3.5
GaV _{1.95}	5.3		73***		
GaV _{2.1-3.5}	6.3-14.45		230-300**		0
GaV ₃		0.4	350***		0
			500***		
GaV _{4.5}	9.15		121*		0
HfNb ₃			>52->102		1.2
HfTa ₃			>28->86		1.2
$Hg_{0.05}Pb_{0.95}$		0.235	23		
$Hg_{0.10}Pb_{0.90}$		0.23	4.3		4.2
$Hg_{0.12}Pb_{0.88}$	~6.75		>13		2.93
$In_{0.84}Pb_{0.16}$	3.45	0.1		0.12	2.76
$In_{0.86}Pb_{0.14}$	3.68	0.1		0.25	2.94
$In_{0.84}Pb_{0.16}$	3.90	0.095		0.35	3.12
$In_{0.82}Pb_{0.18}$	4.2	~0.17	0.55	2.65	
$In_{0.81}Pb_{0.19}$		0.155	3.7		4.2
$In_{0.81}Pb_{0.19}$			2.8	5.5	4.2
$In_{1.000}Te_{1.002}$	3.5-3.7		1.2*		0
$In_{0.95}Ti_{0.05}$		0.263	0.263		3.3
$In_{0.90}Ti_{0.10}$		0.257	0.257		3.25
$In_{0.83}Ti_{0.17}$		0.242	0.39		3.21
$In_{0.75}Ti_{0.25}$		0.216	0.50		3.16
LaN	1.35	0.45		>25	0.76
La_2S_4	6.5	~0.15	>25		1.3
La_2Se_4	8.6	~0.2	>25		1.25
$Mo_{0.51}Re_{0.49}$	11.1		14-21	22-33	4.2
			18-28	37-43	1.3
			14-20	20-37	4.2
			19-26	26-37	1.3
$Mo_{0.620.05}Re_{0.395}$	10.6		~75*		0
$Mo_{0.95}Te_{0.05}$		0.028	98.7*		0
$Mo_{0.16}Ti_{0.84}$	4.18		36-38		3.0
$Mo_{0.91}Ti_{0.09}$	2.95	0.060	~15		4.2
$Mo_{0.1-0.5}U_{0.9-0.7}$	1.85-2.06		>25		
$Mo_{0.17}Zr_{0.83}$			~30		
$N_{12.8}W_{0.2}$	15.2		>9.5		13.2
NNb (wires)	16.1		153*		0
			132		4.2
			95		8
			53		12
NNb_2O_{1-x}	13.5-17.0		~38		
NNb_2Zr_{1-x}	9.8-13.8		4- >130		4.2
$N_{0.83}Nb_{0.85}Zr_{0.15}$			>130		4.2
$Nb_{0.01}Pb_{0.99}$		0.19	6.0		
$Nb_{0.018}Pb_{0.982}$		0.28	2.05		

†w/o denotes weight percent.

HIGH CRITICAL MAGNETIC-FIELD SUPERCONDUCTIVE COMPOUNDS AND ALLOYS (Continued)

Substance	T_c , °K	H_{c1} , kg	H_{c2} , kg	H_{c3} , kg	T_{max} , °K†
Nb	9.15		2.020		1.4
			1.710		4.2
Nb		0.4-1.1	3-5.5		4.2
Nb (unstrained)		1.1-1.8	3.40	6-9.1	4.2
Nb (strained)		1.25-1.92	3.44	6.0-8.7	4.2
Nb (cold-drawn wire)		2.48	4.10	≈10	4.2
Nb (film)			>25		4.2
NbSe			>30		
Nb ₃ Sn		0.170	221		4.2
			70		14.15
			54		15
			34		16
			17		
Nb _{0.1} Ta _{0.9}		0.084	0.154		4.195
Nb _{0.3} Ta _{0.8}			10		4.2
Nb _{0.65} -0.73Ta _{0.02} -0.10Zr _{0.23}			>70->90		4.2
Nb ₁ Ti _{1-x}			148 max.		1.2
			120 max.		4.2
			23		1.2
Nb _{0.335} U _{0.775}		1.98	127 max.		1.2
Nb ₂ Zr _{1-x}			94 max.		4.2
O ₂ SrTi	0.43	.0049*	.504*		0
O ₂ SrTi	0.33	.00195*	.420*		0
PbSb _{1-x} (quenched)			>1.5		4.2
PbSb _{1-x} (annealed)			>0.7		4.2
PbSb _{2.8-x} (quenched)			>2.3		4.2
PbSb _{2.8-x} (annealed)			>0.7		4.2
Pb _{0.871} Sn _{0.129}		0.45	1.1		
Pb _{0.945} Sn _{0.055}		0.53	0.56		
Pb _{1-0.25} Tl _{0-0.74}	7.20-3.68		2-4.9*		0
PbTi _{1-x}	6.73		4.5*		0
Rc _{0.26} W _{0.74}			>30		
Sb _{0.93} Sn _{0.07}			158***		3.7
SiV ₁	17.0	0.55	0.005		
Sn _{0.7} Te _{1-x}		0.00043-	0.005-		0.012-
		0.00236	0.0775		0.079
Ta (99.95%)		0.425	1.850		1.3
		0.325	1.425		2.27
		0.275	1.175		2.66
		0.090	0.375		3.72
			3.55		4.2
Ta _{0.5} Nb _{0.5}			>14-138		1.2
Ta _{0.45} -0.7Ta _{0.35} -1	4.4-7.8		138		1.2
Ta _{0.5} Ti _{0.5}					0
Tc	~3.3	0.25*			4.2
Tc _{0.1} W _{1-x}	5.75-7.88		8-44		4.2
Ti				2.7	0
Ti _{0.13} V _{0.25}	5.3	0.029*	199*		0
Ti _{0.775} V _{0.225}	4.7	0.024*	172*		0
Ti _{0.813} V _{0.185}	7.07	0.050	~34		4.2
Ti _{0.516} V _{0.484}	7.20	0.062	~28		4.2
Ti _{0.413} V _{0.585}	7.49	0.078	~25		4.2
Ti _{0.13} V _{0.88}			173		4.2
Ti _{0.40} V _{0.60}			14.3	28.1	4.2
Ti _{0.06} V _{0.94}			8.2	16.4	4.2
Ti _{0.03} V _{0.97}			3.8	12.7	4.2
Ti ₁ V _{1-x}			108 max.	6.8	1.2
V	5.31	~0.8	~3.4		1.79
		~0.75	~3.15		2
		~0.45	~2.2		3
		~0.30	~1.2		4
V _{0.26} Zr _{0.74}	≈5.9	0.238			1.05
		0.227			1.78
		0.185			3.04
		0.165			3.5
W (film)	1.7-4.1		>34		1

†Temperature of critical field measurement.

*Extrapolated.

**Linear extrapolation.

***Parabolic extrapolation.

TABLES OF PROPERTIES OF SEMICONDUCTORS

Compiled by Dr. Brian Randall Pamplin

The term "semiconductor" is applied to a material in which electric current is carried by electrons or holes and whose electrical conductivity when extremely pure rises exponentially with temperature and may be increased from this low "intrinsic" value by many orders of magnitude by "doping" with electrically active impurities.

Semiconductors are characterised by an energy gap in the allowed energies of electrons in the material which separates the normally filled energy levels of the *valence band* (where "missing" electrons behave like positively charged current carriers "holes") and the *conduction band* (where electrons behave rather like a gas of free negatively charged carriers with an effective mass dependent on the material and the direction of the electrons' motion). This energy gap depends on the nature of the material and varies with direction in anisotropic crystals. It is slightly dependent on temperature and pressure, and this dependence is usually almost linear at normal temperatures and pressures.

The data is presented in three tables. Table I "General Properties of Semiconductors" lists the main crystallographic and semiconducting properties of a large number of semiconducting materials in three main categories; "Tetrahedral Semiconductors" in which every atom is tetrahedrally co-ordinated to four nearest neighbour atoms (or atomic sites) as for example in the diamond structure; "Octahedral Semiconductors" in which every atom is octahedrally co-ordinated to six nearest neighbour atoms—as for example in the halite structure; and "Other Semiconductors".

Table II gives more detailed information about some better known semiconductors, while Table III gives some information about the electronic energy band structure parameters of the best known materials.